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ON THE STRUCTURE OF 2-p-NITROPHENYLINDANE-1,3-DIONE

A. Arens, O. Neilands, and
Academician AN LatvSSR G. Vanags

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In our study of amino derivatives of 2-arylindane-1,3-diones, we included 2-p-nitrophenylindane-1,3-dione (NPI) (I) in the scope of our investigations. This compound was of interest in that, in contrast to the colorless 2-phenylindane-1,3-dione, it is a dark red substance. 2-Chloro- and 2-bromo-NPI are colorless, bis-p-nitrophenylindane-1,3-dione is also colorless, while 2-amino derivatives of NPI are yellow or orange substances like the amino derivatives of 2-phenyl- and 2-anisylindane-1,3-dione [1-4].

It appeared of interest to determine the cause of the color of NPI. To explain this phenomenon only by the empirical fact that the introduction of nitro groups deepens the color of many compounds would be wrong, because it is known that even 2,4-dinitrophenylindane-1,3-dione is scarcely colored [5]. It has been reported in the literature [6, 7] that phenylindanediones having a substituent (Cl, Br, I) in the para position of the phenyl radical exhibit polychromism. The color of these compounds differs depending on the nature of the solvent from which the compounds are prepared: they crystallize as red substances from polar solvents, while nonpolar solvents yield colorless crystals. These compounds exhibit thermochromism. The red forms are converted to the colorless forms during melting-point determinations. There are indications [7] that the red form of NPI is stable and does not change under the influence of temperature or of the solvent. The change in color of arylindanediones in polar solvents is explained by some authors as being due to a shift of the keto–enol tautomeric equilibrium toward the enol form (II) [7]. An elevated temperature and solvents of low polarity apparently favor the reverse process – the formation of the diketo form (I). However, it is impossible not to take into account the possibility that NPI may exist in the valence structures (III) and (IV). In order to resolve this question, we investigated the ultraviolet and infrared spectra of NPI and certain of its derivatives which were conveniently available. We also investigated the methyl ether of its enol form, which was prepared by the action of an ether solution of diazomethane on NPI (an orange substance with an m. p. of 190-192°; found, %: N 5.24; calculated for $C_{16}N_{11}O_4N$, %: N 4.98).

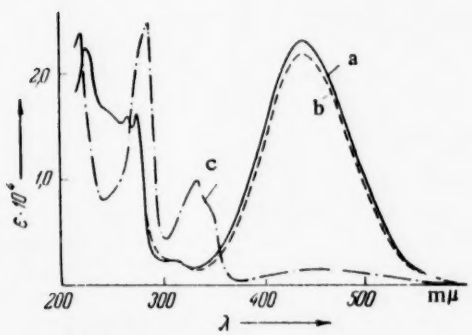
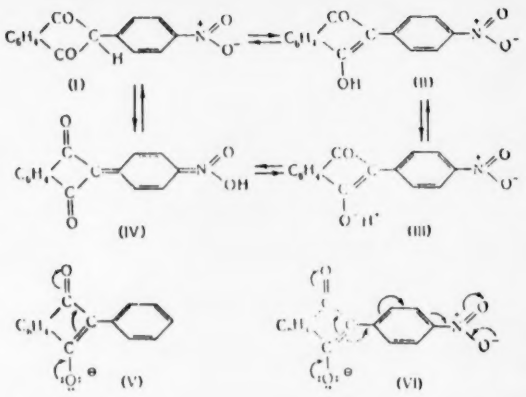


Fig. 1. U. v. absorption spectra in absolute methanol; a) NPI, b) Na salt of NPI, c) Na salt of 2-phenylindanedione.

The absorption curves in the ultraviolet region are identical for NPI and its Na salt dissolved in absolute methanol (Fig. 1). It is evident that the electronic structure of NPI in solution is the same as the electronic structure of its anion. Consequently, NPI is dissociated in absolute methanol. A comparison of the u. v. spectra of the structurally similar Na salts of 2-phenylindane-1,3-dione and



NPI shows that the absorption of these enolate anions differs. This is quite understandable, because leveling out of the electron density in the 2-phenylindane-1,3-dione anion proceeds chiefly toward the carbonyl group (V).

In the case of enolate anion (VI), leveling out of the electron density takes place toward the nitro group owing to the presence of a system of conjugated double bonds. Lengthening of the conjugated system causes an intense absorption at 440 mμ (ϵ = 22200).

The u. v. spectrum of NPI in dichloroethane yields an absorption curve characteristic of diketo forms (Fig. 2), and it is characterized by a λ_{max} at 229 mμ and, correspondingly, an ϵ of 43000. The implications of the i.r. spectrum are in agreement with those of the u.v. spectra. The infrared spectrum, which was obtained using a saturated solution of NPI in dichloroethane, was characterized by two carbonyl group frequencies at 1717 and 1750 cm^{-1}. For the 2-bromo-2-anilino and 2-piperidino derivatives of NPI, in which the diketo form is fixed, absorption due to carbonyl groups is observed at, respectively, 1718 and 1750 cm^{-1}, and 1707 and 1747 cm^{-1}, and 1705 and 1742 cm^{-1}.

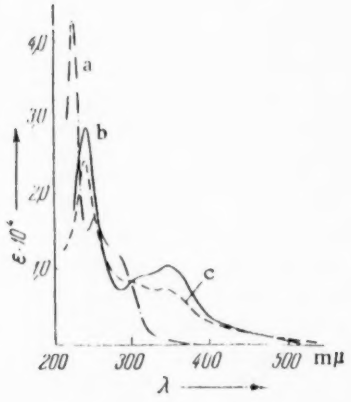


Fig. 2. U. v. absorption spectra: a) NPI in dichloroethane, b) methyl ether of NPI in dichloroethane; c) methyl ether of NPI in absolute methanol.

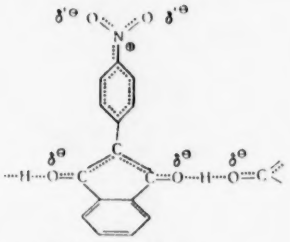
Moreover, it should be noted that an 0.0001 M solution of NPI in dichloroethane is completely colorless. When a suspension of red NPI in chloroform or dichloroethane in a sealed vessel is allowed to stand at room temperature, the red form is gradually converted, on prolonged standing, to the crystalline colorless form, which is undoubtedly the diketo form. During the process of separation from solution, it is reversibly converted to the red form. These data refute the opinion, expressed in the literature, that NPI exists only in the red form, which is not reciprocally convertable to the colorless form [7]. It is evident that NPI is in no wise distinguishable from other 2-phenylindane-1,3-diones which are substituted in the para position with electrophilic substituents. The red form is only the more stable form.

The u.v. spectrum of the methyl ether of the enol form of NPI in absolute methanol differs substantially from the spectrum of NPI itself. In dichloroethane solution, the enol ether has λ_{max} = 245 mμ (ϵ = 29000). For the enol ether in methanol solution, there is a small shift of the K-band toward the lower wave lengths (λ_{max} = 242 mμ ; ϵ = 24000). The infrared spectrum of a 0.01 M solution of the methyl ether of the enol form in dichloroethane confirms that the proposed enol ether structure is correct, because CO group absorption at 1700 cm^{-1}, a band at 1622 cm^{-1} due to the double bond in the five-membered ring, and ν_{NO_2} (asym.) at 1522 cm^{-1} are observed. The higher values of $\nu_{C=O}$ can be ascribed to straining of the five-member ring, which usually increases vibration of the CO group somewhat [9].

The infrared spectrum of a paraffin-oil suspension of the red form of NPI, which has been recrystallized from glacial acetic acid, indicates that this form does not exist in the diketo form (I), because no CO group

absorption is observed. If the sample is recrystallized from water, then, in addition to the other frequencies, CO bands of average intensity appear at 1700 and 1735 cm^{-1}. We feel that partial conversion to the diketo form takes place under the influence of the solvent, since when dried (~140°, 2 hours), the two samples are equivalent. The i.r. data provide no basis on which to assume that the red form of solid NPI is the enol form (II). We were not able to determine the absorption of the enol hydroxyl. Its spectrum has little in common with the spectrum of the enol ether. The data obtained force us to reject the structure of a diketonitronic acid, because absorption characteristic of an α,β-unsaturated diketo group is not observed. The spectrum of red NPI is very similar to that of its sodium salt. The overall picture presented by the spectrum in the double bond region is thereby complicated, which makes it difficult to speak unequivocally of characteristic frequencies of individual groups. The very intense, broad absorption at 1514-1529 cm^{-1}, which is typical of the 2-phenylindanedione enolate anion, was not observed in the spectrum, although absorption was noted in the region of 1510 cm^{-1}. The substance absorbed intensely in the regions of 1340-1350 cm^{-1} and 1560-1570 cm^{-1}.

The infrared spectroscopic data thus show that the red form of NPI probably exists as an ionized form with an equalized electronic structure. As has been pointed out in the literature of acetylacetone tautomerism [8], it is difficult to speak of characteristic group frequencies in these systems.



VII ($\delta' > \frac{1}{2}$; $2\delta + 2\delta' = 2$)

We proposed that in the present case, the proton in the crystal lattice is trapped in the electron field of the carbonyl groups of two neighboring molecules (VII), and equalization of the electron density proceeds mainly in the direction of the carbonyl groups. In a similar manner, it has been assumed that in the case of diquinolyl-(2)-methane, the labile proton is tightly held in the field of the free electron pairs of the two nitrogen atoms of a single molecule [10].

Thus the investigation of NPI has shown that NPI has a very mobile system, which in polar solvents and, probably, also in the solid form, exists as an anion with an equalized electronic structure and is capable of reciprocal conversion. In solvents of low polarity, it exists in the colorless, diketo form. The NPI anion exhibits dual reactivity: thus with diazomethane it yields the methyl ether of the enol form, and with bromine and chlorine it yields the 2-bromo and 2-chloro derivatives.

We consider that the red form of other presently well known 2-arylindane-1,3-diones with electrophilic substituents in the para position of the phenyl radical possess the properties and structural peculiarities of NPI.

The ultraviolet spectra were obtained by A. Grinval'de and M. Tiltin'sh, for which we express our appreciation.

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*See C. B. translation.

HEATS OF COMBUSTION OF 1,1-DIMETHYL-2-ALKYLCYCLOPROPANES

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(Presented by Academician A. N. Nesmeyanov, December 22, 1959)
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Original article submitted December 16, 1959

The existence of accurate experimental data on the heats of combustion of some of the alkylcyclohexanes and alkylcyclopentanes has made it possible to calculate, with a considerable degree of accuracy, the heats of combustion of the remaining members of the respective homologous series, including both compounds with normal and those with branched side chains [1, 2]. At the present time, such calculations cannot be carried out for cyclopropane hydrocarbons, since there are almost no accurate experimentally determined heats of combustion. The only reliable value is that for gaseous cyclopropane [3]. The remaining heats of combustion [4-6] are not very reliable. It may also be mentioned that thermochemical data for cyclopropane hydrocarbons are of considerable practical and theoretical interest.

The present communication reports the results of determinations of the heats of combustion of three 1,1-dimethyl-2-alkylcyclopropanes in the liquid state, and formulas are given for calculating the heats of combustion of all the compounds of this homologous series. The method used to determine the heats of combustion has been described earlier [7]. A calorimeter with an isothermal jacket was used. The liquid samples, which were contained in sealed, thin-wall glass ampoules, were burned in the calorimeter bomb in an excess of oxygen. The initial temperature was 25°. A mercury thermometer was used for the temperature measurements; the temperature readings were made with an accuracy of $(3 \cdot 10^{-4})°$. The calorimeter constants were determined by a standard run with benzoic acid, the heat of combustion of which was taken as 6322.8 cal/g (weighed in air) at 25° (1 cal = 4.1840 abs. joules). Iron wire was used to initiate combustion. The heats of formation of Fe_2O_3 and the nitric acid solution in the bomb were taken as 1793 cal/g and 13.80 kcal/mole, respectively. As a rule, the weight of the sample was determined by the difference in the weights of the empty and filled ampoule with an accuracy of $2 \cdot 10^{-5}$ g, and the sample weight was 0.2 to 0.3 g. In the case of the low-boiling 1,1-dimethyl-2-ethylcyclopropane, the weight of substance burned was found from the results of the analysis of the combustion products for CO_2. The materials were synthesized and purified by the method previously described [8]. The absence of alkene impurities in the preparations was shown by Raman spectroscopy.

1,1-Dimethyl-2-ethylcyclopropane, C_7H_{14} (mol. wt. 98.189). The preparation was purified by three and four distillations over metallic sodium. The constants of the material were not changed by the last distillation: b.p. 78.75°/746; d_4^{20} 0.7105; n_D^{20} 1.3960; microanalysis results (in %): C 85.95; H 14.12, (theoretical for all three compounds: C 85.63; H 14.37).

1,1-Dimethyl-2-n-propylcyclohexane, C_8H_{16} (mol. wt. 112.216). After both the fifth and the sixth distillations over metallic sodium, the preparation had the following constants: b.p. 105.5°; d_4^{20} 0.7297; n_D^{20} 1.4060. Microanalysis results (in %): C 85.96; H 14.17.

1,1-Dimethyl-2-n-hexylcyclopropane, $C_{11}H_{22}$ (mol. wt 154.297). After both the fourth and fifth distillations, the material had the following constants: b. p. 176.5°/736; d_4^{20} 0.7612; n_D^{20} 1.4240. Microanalysis results (in %): C 85.74; H 14.32.

TABLE 1

Heats of Combustion of 1,1-Dimethyl-2-n- alkylcyclopropanes, $-\Delta H_c^0$, at 25° and 1 atm., in kcal/mole

1,1-Dimethyl-2-ethylcyclopropane	1,1-Dimethyl-2-propylcyclopropane	1,1-Dimethyl-2-hexylcyclopropane *
Third distillation	Fifth distillation	Fourth distillation
1115.5	1271.2	1740.3
1115.2	1271.2	1739.9
1115.0	1272.6	1739.4
1114.6	1270.8	1740.0
1114.7	1270.4	
Fourth distillation	Sixth distillation	Fifth distillation
1115.1	1271.2	1739.7
1115.0	1271.1	1741.4
1114.9	1271.1	1739.7
		1739.9
1115.0 ± 0.2** (±0.02%)	1271.2 ± 0.4 (±0.03%)	1739.9 ± 0.4 (±0.03%)

*Table 1 presents only the results of ten of the nineteen determinations made, since combustion was incomplete in the remaining experiments.

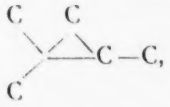
**In all of the data presented in this paper, the indicated errors are average deviations from the arithmetic mean.

Table 1 presents the heats of combustions of the three cyclopropanes determined after two successive distillations. It may be seen from these data that the last distillation brought about no change in the heat of combustion of any of these hydrocarbons.

Using the additive method and the notation for the different types and subtypes of bonds developed by V. M. Tatevskii [1, 2], the general formula for calculating the heat of combustion of 1,1-dimethyl-2-alkylcyclopropanes may be written in the following form:

$$-\Delta H_{C_nH_{2n}} = c' + \sum n_{ij}A_{ij}, \tag{1}$$

where c' is the incremental heat of combustion obtained by summing the bonds in the group



and $\Sigma n_{ij}A_{ij}$ relates to the substituting alkyl radical, normal or branched. For 1-1-dimethyl-2-n-alkylcyclopropanes (the alkyl may be any radical beginning with ethyl, i.e., $n \geq 7$, Eq.(1) takes the form:

$$\Delta H_{C_nH_{2n}} = c' + \sum n_{ij}A_{ij} = I_{2'3'} + I_{2'4'} + I_{3'4'} + 2y_{14'} + y_{23'} + (n-7)A_{22} + A_{21}, \tag{2}$$

where I_{ij} are coefficients relating to bonds in the ring, and y_{ij} relates to the ring–side chain bonds (the sum of which constitutes c'). The remaining terms refer to the bonds in the substituting alkyl radical, and are included

in the sum $n_{ij}A_{ij}$. The experimental data are still insufficient for calculation of I_{ij} and y_{ij}, but A_{22} and c' can be calculated from the data obtained in the present work. The value of A_{22}, found from the heats of combustion of 1,1-dimethyl-2-ethyl- and 1,1-dimethyl-2-n-hexylcyclopropane $A_{22} = 1/4\ (1739.9-1115.0) = 156.23$ kcal/mole, is in agreement with the literature value of 156.231 kcal/mole for alkanes, alkylcyclopentanes, and alkylcyclohexanes [1]. The values of A_{22} calculated by the same method for other physicochemical properties of compounds of this series, properties such as heat of formation ($-\Delta H^0_f$), molar refraction (R_M) and molar volume (V_M), are also in agreement with the literature values. Table 2 presents examples of this agreement.

TABLE 2

Coefficient	$-\Delta H^0_c$		$-\Delta H^0_f$		R_M		V_M	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.	Exp.	Lit
A_{22}	156,23	156,231	6,13	6,138	4,64	4,643	16,27	15,96
c'	851,74	—	6,96	—	25,19	—	96,86	—

Using the values of the heat of combustion of 1,1-dimethyl-2-ethyl- and 1,1-dimethyl-2-n-hexylcyclopropane and the values obtained for A_{22}, heats of combustion were calculated for 1,1-dimethyl-2-propyl-, 1,1-dimethyl-2-n-butyl-, and 1,1-dimethyl-2-n-amylcyclopropane. The heats of combustion ($-\Delta H^0_c$) of these compounds and the heats of formation ($-\Delta H^0_f$) are presented in Table 3. The values of $-\Delta H^0_f$ were calculated using $-\Delta H^0_{fCO_2}$ (gas) = 94.052 kcal/mole and $-\Delta H^0_{fH_2O}$ (liq) = 68.317 kcal/mole.

TABLE 3

Heats of Formation and Heats of Combustion of 1,1-Dimethyl-2-n-alkylcyclopropanes at 25° and 1 atm, in kcal/mole

	Compound	$-\Delta H^0_{exp}$	$-\Delta H^0_{calc}$	$-\Delta H^0_f$
1	1;1-Dimethyl-2-ethylcyclopropane	1115.0	–	21.6
2	1,1-Dimethyl-2-propylcyclopropane	1271.2	1271.2	27.8
3	1,1-Dimethyl-2-butylcyclopropane	–	1427.4	33.9
4	1,1-Dimethyl-2-amylcyclopropane	–	1583.6	40.0
5	1,1-Dimethyl-2-hexylcyclopropane	1739.9	–	46.2

As the data of Table 3 show, the calculated and experimental values of the heat of combustion of 1,1-dimethyl-2-n-propylcyclopropane are in agreement.

It is known that the presence in the cycloparaffin molecule of a relatively strain-free five-member or six-member ring has practically no effect on the contribution of the side chain to the properties here considered [1]. In the case of the strained three- or four-member rings, the question has remained unanswered up to the present. It follows from the data obtained in the present work that the presence of cyclopropane ring has not effect on the nature of the bonds in the substituting radical beginning with ethyl. This conclusion can apparently be extended to alkylcyclobutane compounds. Thus, heats of combustion may be calculated for compounds of the 1,1-dimethyl-2-n-alkylcyclopropane series (n-alkyl and other higher substituents) by means of Eq. 3:

$$-\Delta H^0_c = 1115{,}0 + (n-7)\,156{,}23, \qquad (3)$$

where $n \geq 7$ is the number of carbon atoms in the molecule.

Heats of formation may be calculated similarly from Eq. (4):

$$-\Delta H_f^0 = 21{,}6 + (n-7)\,6{,}13. \qquad (4)$$

Using the heats of combustion of 1,1-dimethyl-2-ethyl-, 1,1-dimethyl-2-n-propyl-, and 1,1-dimethyl-2-n-hexylcyclopropanes and the literature values for A_{22} (156.231 kcal/mole) and A_{21} (263.238 kcal/mole), we calculated the value of the increment c' which enters into Eqs. (1) and (2). The value thus obtained was c = 851.74 kcal/mole. Values of c' calculated for $-\Delta H_f$, R_M, and V_M, are presented in Table 2. It now appears possible to calculate heats of combustion of not only normal, but also of branched* 1,1-dimethyl-2-alkylcyclopropanes. In this case, Eq. (1) has the form

$$-\Delta H_c = 851.7 + \sum n_{ij} A_{ij} \quad \text{for} \quad n \geqslant 7. \qquad (5)$$

Values of the A_{ij} coefficients for C–C bonds of the different subtypes in branched alkanes may be obtained from the literature [1].

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*For branching beginning with the second carbon atom of the alkyl radical.

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THE INTERACTION OF FLUOROOLEFINS WITH NITROSYL FLUORIDE

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Nitrosyl fluoride was first prepared by Ruff in 1905 [1]. However, up to the present, it has been studied only with respect to its physical properties [2] and its reaction with certain inorganic substances (boron, silicon, red phosphorus, AsF_3, H_2SO_4, and others [1, 3] and with benzene [4].

We have now shown that nitrosyl fluoride readily reacts with fluoroolefins, adding across the carbon–carbon double bond.* Thus, the interaction of nitrosyl fluoride with perfluoroisobutylene gave tert-nitrosoperfluoroisobutane (b. p. +24°) in quantitative yield

$$\begin{matrix} CF_3 \\ CF_3 \end{matrix}\!\!>\!C=CF_2 + FNO \rightarrow \begin{matrix} CF_3 \\ CF_3 \end{matrix}\!\!>\!C(N=O)-CF_3.$$

2-Nitrosoperfluoropropane (b. p. −13°) was obtained from perfluoropropylene and FNO

$$CF_3-CF=CF_2 + FNO \rightarrow CF_3-\underset{\displaystyle N=O}{\underset{|}{CF}}-CF_3.$$

Perfluoroethylene also reacts with nitrosyl fluoride, but is was not possible to isolate perfluoronitrosoethane from the reaction products, since under the reaction conditions, this compound reacts with excess perfluoroethylene, giving perfluoro-2-ethyl-1,2-oxazetidine, which is the major reaction product

$$CF_2=CF_2 + FNO \rightarrow [CF_3-CF_2-NO] \xrightarrow{+CF_2=CF_2} CF_3-CF_2-\underset{\displaystyle CF_2-CF_2}{\underset{|\quad|}{N-O}}.$$

The formation of oxazetidines was observed by Hazeldine [5] during the reaction of trifluoronitrosomethane with tetrafluoroethylene and other fluoroolefins.

The reaction between nitrosyl fluoride and trifluoroethylene unexpectedly led to the formation of perfluoronitrosoethane, a blue gas with a b. p. of −42 to −43°. The formation of this compound can be explained by the following sequence of reactions:

$$CF_2=CFH + FNO \rightarrow [CF_3-CFH-N=O] \rightarrow \left[CF_3-C\begin{matrix}F\\ \diagdown\\ N-OH\end{matrix}\right] \rightarrow$$

$$\xrightarrow{+HF} [CF_3-CF_2-NH-OH] \xrightarrow[-H_2O]{O} CF_3-CF_2-N=O.$$

*The nitrosyl fluoride was prepared by reacting gaseous fluorine with nitric oxide.

The reaction between nitrosyl fluoride and vinylidene fluoride is still more complex. The only product of this reaction was a compound with a b. p. of 80° and an empirical formula of $(C_2F_3H_2ON)_x$. An investigation of the properties of this compound suggested the following structure:

$$CF_3-CH_2-N-O$$
$$\quad\quad\quad\quad\quad|\quad\quad|$$
$$CF_3-CH-N-OH.$$

It was probably formed as a result of the following reactions:

$$CF_2=CH_2+FNO\rightarrow[CF_3-CH_2-N=O];$$
$$2(CF_3-CH_2-N=O)\rightarrow CF_3-CH_2-N-O$$
$$\quad\quad\quad\quad\quad

on a shaker at room temperature for 24 hours. The tube was then opened, and the unreacted starting materials were were distilled. The residue was a dark blue liquid with a b. p. of 24°/760 mm, d_4^0 1.6630. Mol. wt.: found, 249; calculated for C_4F_9NO, 249.

Found %: C 19.40; N 5.28; F 69.21, Calculated %: C 19.28; N 5.62; F 68.67.

Perfluoropropylene and FNO. A. The charge to the steel reaction tube consisted of 2 g of activated carbon impregnated with calcium sulfate, 25 ml of perfluoropropylene, and 10 ml of nitrosyl fluoride. The tube was heated at 140-150° for 7 hours. The following compounds were obtained by distillation of the reaction mixture:

1) Perfluoronitrosopropane – a blue gas with a b. p. of –13°. Mol. wt.: found, 197; calculated for C_3F_7NO, 199.

Found %: N 6.66; F 67.06. Calculated %: N 7.03; F 66.83.

2) Perfluoro-2-propanol nitrite – a yellow liquid with a b. p. of 25°/749 mm. The liquid decomposed with the evolution of nitrogen oxides when poured into water. The water was extracted with ether; the residue remaining after distillation of the ether proved to be perfluoroacetone hydrate. This was a colorless liquid with a b. p. of 50°/90 mm; d_4^{20} 1.3950; n_D^{20} 1.3252. Literature values [7]: b. p. 57°/93 mm d_4^{20} 1.4085; n_D^{20} 1.3288. This compound formed a semicarbazone with an m. p. of 153°. Literature value [7]: m. p. 153°.

Found %: C 19.48; H 2.20; N 16.81. Calculated %($C_4H_5F_6N_3O_2$): C 19.91; H 2.04; N 17.12.

B. The charge to the steel tube consisted of 25 ml of perfluorpropylene and 10 ml of nitrosyl fluoride. The tube was heated at 100-110° for 7 hours. After distillation of the unreacted starting material, the reaction mixture was poured into ice water. A part of the product decomposed with the evolution of nitrogen oxides, and a heavy, blue liquid remained. The aqueous solution was extracted with ether. α-Nitroperfluoropropionic acid was obtained upon distillation of the ether. This was a colorless liquid with a b. p. of 56°/35 mm; d_{20}^{20} 1.4866; n_D^{20} 1.3578. Literature values [6]: b. p. 119°; d_4^{20} 1.638; n_D^{20} 1.3560. The molecular weight was determined by titration with a base; found, 194; calculated for $C_3HF_4NO_4$, 191. The blue liquid was nitronitrosoperfluoropropane; b. p. 53-54°; d_4^{20} 1.6507. Mol. wt.: found, 227; calculated for $C_3F_6N_2O_3$, 226.

Found %: C 16.02; N 12.00; F 50.50. Calculated %: C 15.92; N 12.39; F 50.44.

Tetrafluoroethylene and FNO. The charge to the steel tube consisted of 2 g of activated carbon impregnated with calcium sulfate, 20 ml of tetrafluoroethylene, and 10 ml of nitrosyl fluoride. The tube was heated at 70-80° for 10 hours. The tube was cooled and opened, the gaseous reaction products were distilled, and the residue was poured into ice water. The resulting oil was separated, dried with sodium sulfate, and distilled. The product was perfluoro-2-ethyl-1,2-oxazetidine – a colorless liquid with a b. p. of 24°/737 mm; d_4^0 1.634; $n_D^0 < 1.3$. Mol. wt.: found (Victor Meyer method), 252; calculated for C_4F_9NO, 249.

Found %: C 19.65; N 5.75; F 68.35. Calculated %: C 19.28; N 6.62; F 68.67.

The wash water was extracted with ether, and the ether was distilled to obtain nitrodifluoroacetic acid – a colorless liquid with a b. p. of 70°/25 mm; d_4^{20} 1.4358; n_D^{20} 1.3660. Literature values [8]: b. p. 72°/25 mm; d_4^{20} 1.4381; n_D^{20} 1.3670. Hexafluoroethane was found in the gaseous reaction products; this was a gas with a b. p. of –79° and an f. p. of –101°. Literature values [9]: b. p. –79°; f. p. –100.6°. F Found, 81.72%; F calculated, 82.61%; mol. wt.: found, 137, calculated, 138.

Trifluoroethylene and FNO. The charge to the steel tube consisted of 10 ml of trifluoroethylene, 5 ml of nitrosyl fluoride, and 20 ml of perfluorocyclobutane. The tube was allowed to stand at room temperature for two days. The tube was then opened, and the gaseous reaction products were condensed and fractionated in a Podbielniak column. The following compounds were found in addition to perfluorocyclobutane: 1) Pentafluoroethane – a colorless gas with a b. p. of –48 to –50° and an m. p. of –103°. Literature values [10]: b. p. –48.5°; m. p. –102°. 2) Perfluoronitrosoethane – a blue gas with a b. p. of –42 to –43°. Mol. wt.: found, 144; calculated for C_2F_5NO, 149.

Found %: C 15.34; N 9.06; F 62.74. Calculated %: C 16.10; N 9.39; F 63.75.

The liquid reaction product (combined product of seven runs) was distilled in a fractionation column. The following products were collected:

1) Trifluoroacetic acid – a colorless liquid with a b. p. of 72°; d_4^{20} 1.542; $n_D < 1.3$. Literature values [11]: d_4^{15} 1.535; $n_D < 1.3$.

Found %: F 49.44. Calculated %: F 50.00

2) Trifluoroacetaldehyde (collected in the trap). This was a colorless gas with a b. p. of −21°. The literature gives a value of −21° for the b. p. [12]. Mol. wt.: found, 98; calculated for C_2F_3HO, 98. This material readily polymerized to beautiful red crystals. When this gas was passed into a solution of 2,4-dinitrophenylhydrazine, a crystalline hydrazone precipitated, the m. p. of which was 150-151°, after recrystallization from alcohol. The literature [12] gives a value of 150-151°.

Found %: N 19.70. Calculated ($C_8H_5F_3N_4O_4$) %: N 20.15.

Vinylidene fluoride and FNO. The charge to the steel tube consisted of 10 ml of vinylidene fluoride, 8 ml of nitrosyl fluoride, and 25 ml of Freon-22. The tube was allowed to stand at room temperature for two days. The tube was opened, and the solvent and unreacted starting materials were distilled, leaving a colorless, mobile liquid which was insoluble in water and in aqueous solutions of alkalies. The product of fusion with dry KOH gave a qualitative reaction for nitrous acid. B. p. 79-80°; d_4^{21} 1.6160; n_D^{21} 1.3437. Mol. wt.: found, 217; calculated for $C_4H_4F_4N_2O_2$, 226. One labile hydrogen atom was found in the compound.

Found %: C 21.52; H 1.85; N 12.75; F 50.73. Calculated %: C 21.24; H 1.89; N 12.39; F 50.44.

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A NEW METHOD FOR THE SYNTHESIS OF 2,2,6,6-TETRAALKYL-3,5-TETRAHYDROPYRANDIONES

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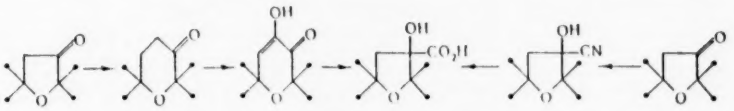
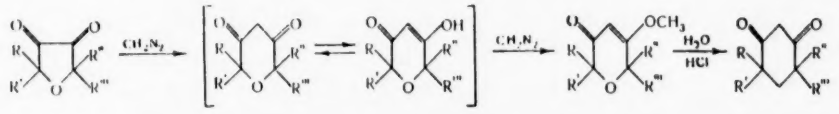
The present article presents the results of an investigation of the reaction of diazomethane with monoketones and α-diketones of the furanidine series.

We have established that the action of diazomethane on 2,2,5,5-tetramethyl-3-furanidone yields 2,2,6,6-tetramethyl-3-tetrahydropyranone and traces of 2,2,6,6-tetramethyl-4-tetrahydropyranone; the best results are obtained by carrying out the reaction in situ using N-nitroso-N-methylurethan or N-nitroso-N-methylurethylan [N-nitroso-N-methyl methylcarbamate] The yield of the major reaction product reaches 55-58%. Proof of the structure of 2,2,6,6-tetramethyl-3-tetrahydropyranone, which is a representative of the previously almost unknown class of tetrahydro-β-pyranones, was by oxidation with selenium dioxide to Δ^4-2,2,6,6-tetramethyl-3-dihydropyranon-4-ol, benzilic acid rearrangement of which led to 3-hydroxy-2,2,5,5-tetramethylfuranidinecarboxylic acid which was identical to the acid prepared from 2,2,5,5-tetramethyl-3-furanidone.



Considering the significant number of diones prepared in the present work, we feel that we have shown that the interaction of 2,2,5,5-tetraalkyl-3,4-furanidinediones with an ether solution of diazomethane proceeds with expansion of the ring between the two carbonyl groups. Under the conditions of the reaction, the resulting 2,2,6,6-tetraalkyl-3,5-tetrahydropyrandiones are enolized and methylated by the excess diazomethane, and, consequently, the products of such reactions are methyl ethers of 2,2,6,6-tetraalkyl-3,5-tetrahydropyrandiones:



These ethers are readily hydrolyzed by heating with hydrochloric acid, yielding, 2,2,6,6-tetraalkyl-3,5-tetrahydropyrandiones; this reaction should be a convenient method for the synthesis of these β-diketones of the tetrahydropyran series.

These β-diketones of the tetrahydropyran series readily form various derivatives; thus, for example, 2,2,6,6-tetramethyl-3,5-tetrahydropyrandione forms a dioxime, the hemibenzilidene derivative is methylated by diazomethane, and the diketone enters into azo coupling reactions [1]. Reduction of the methyl ether of 2,2,6,6-tetramethyl-3,5-tetrahydropyrandione with lithium aluminum hydride and subsequent hydrogenation over

TABLE 1

Methyl ether of 2,2,6,6-tetraalkyl-3,5-tetrahydropyrandione	Yield, %	M. p., °C (after sublimation)	C, %		H, %	
			found	calc.	found	calc.
2,2,6,6-Tetramethyl ($C_{10}H_{16}O_3$)	46	74—75	65,26 65,20	65,19	8,79 8,93	8,75
2,6-Dimethyl-2,6-diethyl ($C_{14}H_{20}O_3$)	41	69,8—71,3	67,67 67,73	67,89	9,50 9,55	9,50
2,2,6,6-Bistetramethylene ($C_{14}H_{20}O_3$)	18,5	46—47	71,15 71,20	71,16	8,65 8,51	8,53
2,2,6,6-Bispentamethylene ($C_{16}H_{24}O_3$)	51,5	124,5—126	72,48 72,61	72,69	9,24 9,26	9,15

platinum gave 2,2,6,6-tetramethyl-3-tetrahydropyranone, which was identical to that obtained from 2,2,5,5-tetramethyl-3-furanidone and diazomethane.

The ultraviolet absorption spectra of methanol solutions of 2,2,6,6-tetraalkyl-3,5-tetrahydropyrandiones and their methyl ethers have an intense maximum in the region of 250 mμ ($\log\epsilon$ 4.6), which indicates considerable enolization of these β-diketones in methanol solution and the absence of intramolecular hydrogen bonding. The ultraviolet absorption spectra of 2,2,6,6-tetraalkyl-3,5-tetrahydropyrandiones in 0.01 N methanolic NaOH have an absorption maximum in the region of 280 mμ ($\log\epsilon$ 4.6), which indicates complete enolization of these diketones in methanol and complete dissociation in methanol solutions of sodium hydroxide.

It should be pointed out that in all cases, with the exception of 2,2,5,5-tetramethyl-3,4-furanidinedione, good yields of the methyl ethers of 2,2,6,6-tetraalkyl-3,5-tetrahydropyrandiones were obtained only when methanol (10% by volume) was added to the reaction mixture. Since 2,2,5,5-tetraalkyl-3,4-furanidinediones exist in the hemiacetal form [2] in methanol solutions, we consider that only this form of 3,4-furanidinediones can react with diazomethane with expansion of the ring. The high yield of the methyl ether of 2,2,6,6-tetramethyl-3,5-tetrahydropyrandione, which was obtained without the addition of methanol, may be explained on the basis that the original 3,4-furanidinedione is very hygroscopic [3] and always contains a certain amount of the hydrated form, which has a structure similar to that of a hemiacetal.

It may be remarked that according to the data of B. Eistert [4], expansion of the ring of triketohydrindane under the influence of diazomethane proceeds only in the complete absence of water or alcohol.

TABLE 2

2,2,6,6-Tetraalkyl-3,5-tetrahydropyrandione (molecular formula)	Yield from pure ether		Yield from crude ether, %	M. p., °C (after sublimation)	C, %		H, %	
	%, based on ether	%based on α-diketone			found	calc.	found	calc.
2,2,6,6-Tetramethyl ($C_9H_{14}O_3$)	92,5	42,5	66	158—158,5	63,31 63,51	63,51	8,42 8,54	8,29
2,6-Dimethyl-2,6-diethyl ($C_{11}H_{18}O_3$)	90	37	44	150,8—151,3	66,52 66,39	66,64	9,09 8,99	9,15
2,2,-Dimethyl-6,6-tetramethylene ($C_{11}H_{16}O_3$)	—	—	40	152,5—153,5	67,41 67,57	67,32	8,34 8,33	8,22
2,2,6,6-Bistetramethylene ($C_{13}H_{18}O_3$)	96,5	18	38	169—170	70,32 70,17	70,24	8,17 8,23	8,16
2,2,-Dimethyl-6,6-pentamethylene ($C_{12}H_{18}O_3$)	—	—	41	161,5—162	68,85 68,90	68,54	8,79 8,69	8,63
2,2,6,6-Bispentamethylene ($C_{15}H_{22}O_3$)	96	49,5	55	193	72,09 72,07	71,97	8,87 8,93	8,86

EXPERIMENTAL

Methyl ethers of 2,2,6,6-tetraalkyl-3,5-tetrahydropyrandiones. To 300 ml (0.171 mole) of an ether solution of diazomethane at 0° was added 30 ml of absolute methanol and, after the solution had been stirred for 15 minutes, a solution of 0.05 mole of the 2,2,5,5-tetraalkyl-3,4-furanidinedione in 50 ml of absolute ether and 10 ml of absolute methanol. The mixture was allowed to stand overnight, and the solvent was then evaporated under vacuum. The residue was dissolved in ether, and, after the solution had been cooled to −70°, the precipitate was filtered. The constants and yields of the resulting methyl ethers are shown in Table 1.

2,2,6,6-Tetraalkyl-3,5-tetrahydropyrandiones. A suspension of 1 g of the pure methyl ether of the 2,2,6,6-tetraalkyl-3,5-tetrahydropyrandione in 5 ml of 19% HCl was heated on a water bath with frequent stirring for several hours. The reaction mixture was cooled, and the diketone was separated. If the ether of the diketone was not separated, and instead the crude reaction mixture formed during the action of diazomethane on the 3,4-furanidinedione was hydrolyzed, the yields of these β-diketones were higher, as may be seen from the data presented in Table 2.

Our heartfelt thanks are due Prof. Yu. K. Yur'ev for his constant attention and interest in the present work.

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ON THE STERIC CONFIGURATION OF THE STEREOISOMERIC 1,4-DIISOPROPYLCYCLOHEXANES

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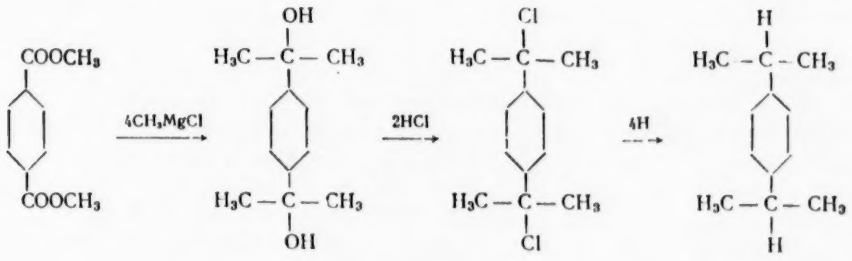
In 1956, we showed that the lower boiling isomer of the stereoisomeric 1,4-diisopropylcyclohexanes has the higher index of refraction and the higher density. However, among the other presently known stereoisomeric 1,4-dialkylcycloalkanes, a higher index of refraction and a higher density are, on the contrary, characteristic of the higher boiling isomers. A preliminary [1] and then a more detailed [2] investigation of the Raman spectra of the stereoisomeric 1,4-diisopropylcyclohexanes and a comparison of these spectra with those of other cis-trans-1,4-dialkylcyclohexanes [3] (including the spectrum of 1,4-dimethylcyclohexane, for which the stereoisomeric configurations of the stereoisomers have been quite reliably proved [4]) showed that the lower boiling 1,4-diisopropylcyclohexane is the cis form. Thus, we have here a peculiar deviation from the rule of Auwers and Skita, which states that the cis form of disubstituted cycloalkanes should boil higher than the trans form. It is well known that some recently appearing reviews of this rule have dealt only with the 1,3-dialkylcyclopentanes [5] and 1,3-dialkylcyclohexanes [4], and failure of this rule in the 1,4-disubstituted cycloalkanes had not been noted until our work. It is true that in 1958, Eliel and Haber [6] observed an infraction of this rule which was completely analogous to that occurring among the 1,4-diisopropylcyclohexanes, but in the case of oxygen derivatives: 2-, 3-, and 4-methylcyclohexanols.

In view of the basic significance of such infractions of the Auwers–Skita rule, we considered it important to undertake more reliable confirmation of the infraction in the case of the 1,4-diisopropylcyclohexanes by increasing the reliability of the synthesis routes in addition to that of the spectroscopic proof, which was mentioned above. The present work was devoted to a solution of this problem.

As starting materials for the synthesis, we selected the dimethyl esters of cis- and trans-hexahydroterephthalic acid, the steric configurations of which, like those of the acids themselves, are known beyond doubt [7, 8]. We intended to convert each of the stereoisomers separately into the corresponding form of 1,4-diisopropylcyclohexane in accordance with the following scheme:



Had the reaction proceeded stereospecifically, a comparison fo the constants of the isomeric hydrocarbons obtained by this route with those of the hydrocarbons previously obtained by close fractionation [1] would have given a final answer with regard to their steric configurations. However, we were able to obtain only the trans form by this route. In the case of the cis form, none of the synthesis steps proceeded stereospecifically, and it was generally not even possible to isolate the corresponding cis-dichloride in a pure form.

A detailed description of the synthesis and properties of the stereoisomeric diols, trans-dichloride, and certain other substances, which were prepared for the first time during this work, will be reported in the future; we shall confine this paper to a brief report of the data. The original dimethyl cis- and trans-hexahydroterephthalates were prepared by hydrogenation of dimethyl terephthalate, separation by freezing, and then careful purification of the trans form (fractional recrystallization; m. p. 70.0-70.5°) and of the cis form; the latter was purified by low-temperature crystallization from ether and vacuum distillation in an efficient column (b. p. 126.9-127.2°/7 mm; f. p. 9.6°; n_D^{20} 1.4590; d_4^{20} 1.1111).

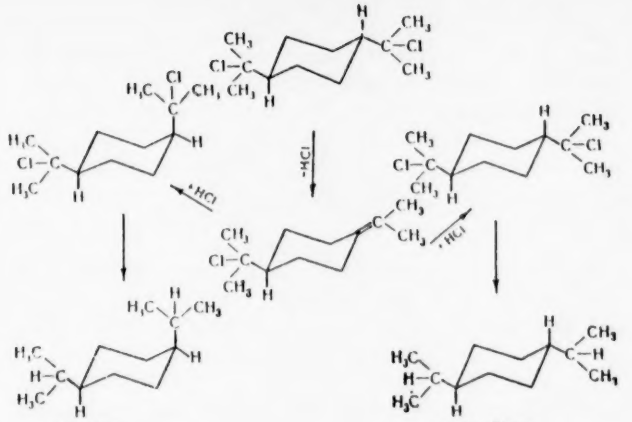
It is curious to note that during this distillation of the stereoisomeric dimethyl hexahydroterephthalates, the pure ester of the cis-acid came over in the first fractions, while the trans-ester crystallized out of succeeding fractions and was also present in considerable amount in the residue. Thus in the present case, the trans form boils above the cis form, in contradiction to the rule of Auwers and Skita, as was the case in the 1,4-diisopropylcyclohexanes [1].

The 1,4-bis(α-hydroxyisopropyl)cyclohexanes were prepared by interaction of the esters of the stereoisomeric acids with a large excess of methylmagnesium chloride or bromide (cis form: m. p. 100.5-100.7°; trans form, m. p. 159.3-159.8°). The corresponding dichlorides were prepared by saturation of methanol solutions of the diols with dry hydrogen chloride. The trans-isomer was obtained in the pure form (m. p. 134.3-135.4°); however, a mixture of the cis- and trans-dichlorides which could not be separated was obtained from the cis-diol.

Replacement of the chlorine by hydrogen proved to be a very difficult problem. Thus, at room temperature, the chlorine in trans-1,4-bis(α-chloroisopropyl)cyclohexane was not replaced by hydrogen either at atmospheric or at elevated (150 atm.) pressure in the presence of Raney nickel, platinum, or palladium, the palladium being deposited on calcium carbonate, which, according to the literature [9], causes elimination of chlorine even from the benzene ring. When the temperature was increased to 50-70° in the presence of these catalysts, the chlorine was not replaced, but was split out as HCl with the formation of diolefins, which were then hydrogenated to yield a mixture of stereoisomers (n_D^{20} 1.4511). The dichloride did not react with magnesium, even in the presence of a large excess of ethyl bromide. Thus, the usual methods for replacement of halogen by hydrogen proved to unsuitable in our case.

In 1949, G. P. Men'shikov, who was studying the structure of the alkaloid heliotrine, successfully eliminated a chlorine atom, which he had previously introduced, by means of the action of an aqueous solution of chromous chloride [10]. This method could not be used in our case owing to the complete insolubility of our dichloride in water; however, we were able to find another, suitable solvent – ethyl acetate. Not only did the dichloride and $CrCl_2$ dissolve readily in this solvent, but so also did $CrCl_3$, from which we prepared $CrCl_2$ directly in the ethyl acetate solution. We were able to carry out the desired reaction at room temperature in this solvent. The constants of the trans-1,4-diisopropylcyclohexane obtained by this route are presented in Table 1. A comparison of these constants with those of the hydrocarbon prepared in our earlier work [1] shows that the determination of the configurations of the stereoisomers by Raman spectroscopy was correct.

The fact that the synthetic preparation differed somewhat in constants from the one obtained by distillation [1], which was of a higher degree of purity, may be explained by the presence in the former of a small amount of the cis-isomer (7-10%). Since the sharp melting points of the diol and dichloride suggest that these compounds could not contain such a large amount of the other form, it may be assumed that the formation of the stereoisomeric impurity probably occurred during the process of eliminating the chlorine. In all probability, partial elimination of hydrogen chloride took place at sites of local overheating during this reaction. The hydrogen chloride, the concentration of which was rather high under the reaction conditions, could then again add across the double bond formed by the original elimination of hydrogen chloride with the formation of cis and trans forms. As a result of subsequent elimination of chlorine, one of these forms gave rise to the stereoisomeric impurity, for example:



cis form trans form

Nevertheless, this side reaction obviously occurs only to a slight extent, and elimination of chlorine leads primarily to the trans-isomer. Thus, our earlier conclusion that the lower boiling 1,4-diisopropylcyclohexane has the cis configuration and the higher boiling isomer has the trans configuration has received additional confirmation.

TABLE 1

Comparison of the Constants of Stereoisomeric 1,4-Diisopropylcyclohexanes

1,4-Diisopropylcyclohexane	B. p., °C/7.5 mm	F. p., °C	n_D^{20}	d_4^{20}
trans-Isomer prepared in the present work	80.1-81.1	−29.7	1.4488	0.8152
trans-Isomer prepared in [1] (99.6% pure)	80.4	−28.0	1.4485	0.8143
cis-Isomer prepared in [1] (99.7% pure)	78.9	−52.9	1.4524	0.8236

EXPERIMENTAL

Solution of $CrCl_3$ in ethyl acetate. The reactants, 30 g of recrystallized potassium dichromate and 180 ml of concentrated hydrochloric acid, were placed in a porcelain casserole, and the mixture was heated on a water bath until evolution of chlorine ceased; during the heating, hydrochloric acid was added as it was consumed. The reaction mixture was then heated to the formation of a viscous, gummy mass, which was transferred, while cooling, to a jar containing 350 ml of dry ethyl acetate free of ethyl alcohol. The chromic chloride dissolved* with the formation of a dark brown solution. It was necessary to filter this solution from the undissolved KCl and to saturate it with dry hydrogen chloride; the color of the solution then changed to a dark raspberry.

Reduction of trans-1,4-bis(α-chloroisopropyl)cyclohexane. The zinc dust, 63 g, was charged to the reaction vessel, which consisted of a 1-liter round bottom, four-neck flask fitted with a stirrer with mercury seal, a dropping funnel, and inlet and outlet tubes for hydrogen; these tubes were isolated from the atmosphere by Tishchenko bottles containing sulfuric acid. The air was purged from the flask with hydrogen, and 165 ml of the solution of $CrCl_3$ in ethyl acetate saturated with HCl was then carefully added from the dropping funnel. When all of the solution had been added and reaction was complete (the solution became a pure sky-blue), the reaction mixture was cooled to room temperature, and a solution of 5.0 g of trans-1,4-bis(α-chloroisopropyl)cyclohexane in 200 ml of ethyl acetate was added. Stirring was continued around the clock for a total of 75 hours, during which time was added 350 ml of a saturated solution of dry HCl in ethyl acetate in 18 additions of 10-20 ml each; during this time, the zinc almost completely dissolved. The reaction mixture was then poured into three volumes of water, and all material boiling up to 100° was distilled off in a Favorskii flask. The distillate was salted out

*If the evaporation was carried out until a dry, solid mass was obtained, solution took place with difficulty, and several days were required.

with potassium carbonate. The ethyl acetate was distilled from the dried upper layer. The distillation was carried out in a small Favorskii flask, into which the solution was continuously fed from a dropping funnel during the distillation. The residue (4.8 g) was combined with a similar residue (3.1 g) from a parallel experiment with 4 g of the dichloride. The combined residue was treated with two 1-ml portions of concentrated sulfuric acid (3 ml of material was absorbed), washed with water, dried, and chromatographed over silica gel. This procedure yielded the fraction (2.45 g) for which the properties are presented in Table 1. The succeeding fraction gave positive reactions for unsaturates and halogen.

The Raman spectrum* of the diisopropylcyclohexane fraction prepared as described above showed all of the lines characteristic of the higher boiling isomer, which was previously assigned the trans configuration; however, according to the spectroscopic data, 7-10% of the cis-isomer was present in all fractions. On the basis of freezing point and the previously determined [1] cryoscopic constant of the trans form (0.043 mole fraction per degree), the content of the cis form was 9%; assuming additivity of the refractive indices and specific volumes, the content of this impurity was 8% according to both properties. The yield of the fraction was 69% of the theoretical, calculated on the dichloride.

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*The spectroscopic analysis was carried out by V. T. Aleksanyan and Kh. E. Sterin (of the Commission for Spectroscopy OFMN [Division of Physical and Mathematical Sciences] AN SSSR), to whom we take this opportunity to express our appreciation.

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THE POLAROGRAPHIC BEHAVIOR OF SODIUM, POTASSIUM, AND LITHIUM BOROHYDRIDES

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In spite of the fact that considerable literature on the borohydrides of the alkali metals exists [1-5], many of their properties, particularly their polarographic behavior, have not been sufficiently studied. Only two papers have been published on the polarography of the borohydrides, and the data of these papers are contradictory and very limited, since they relate only to a single representative of this class of compounds, $NaBH_4$. R. L. Pecsok [6], studying the hydrolysis and oxidation of sodium borohydride by a polarographic method, obtained (at a pH > 9) an anode wave with $E_{1/2} = +0.105 - 0.013$ v, while in somewhat earlier work, E. D. Marschall and R. A. Widding [7] obtained $E_{1/2} = -0.6$ v (n. c. e.). Pecsok explained this considerable discrepancy by the presence of impurities in the preparation available to the earlier authors, but he used in his own work a technical product with a purity of about 95%. Though he evidently recognized the reversibility of the anodic oxidation of $NaBH_4$, Pecsok nevertheless used the Ilkovic equation and arrived at the conclusion that eight electrons are involved in the reaction: $BH_4^- + 8OH^- = BO_2^- + 6H_2O + 8\,e$.

During the course of work on the application of borohydrides to analytical chemistry [8], a study was undertaken in our laboratory, of the polarographic behavior of $NaBH_4$, KBH_4, and $LiBH_4$. Both technical (about 80% purity)* and purified preparations were used in the work; the purified samples were prepared by the method described in reference [8] and contained more than 98% borohydride.

The samples were polarographed using a Heyrovsky micropolarograph, Model M-102, with a dropping mercury electrode (capillary constant $K = 3.14^{2/3} \cdot 2.6^{1/6} = 2.50$). A precision voltmeter was used to measure the potentials. A careful examination of the anodic and cathodic regions of all of the polarographic curves over the interval from + 0.2 v to − 2.0 v showed that the solution of $NaBH_4$ in NaOH has only a single anode wave with $E_{1/2} = -0.65$ v. This wave decreased over a period of time with the decomposition of the $NaBH_4$, and finally disappeared entirely. Decomposition of the borohydride by boiling and by acidification of the solution also caused the wave to disappear. It was equally well expressed in both the case of the technical product and in the case of the purified $NaBH_4$. The presence of impurities, chiefly the alcoholate, in the former in no wise showed up on the polarograms. Nor did a specially prepared alcoholate give a curve. That the observed wave belonged to the BH_4^- ion was then confirmed by experiments with purified and unpurified KBH_4 and $LiBH_4$ in solution in KOH and LiOH, respectively. Both of these compounds gave the same wave, and they behaved polarographically in the same manner as $NaBH_4$ (Fig. 1 and Table 1). The position and character of the wave was practically unchanged with variations in the borohydride concentration and with changes in the composition of the supporting electrolyte – introduction of chlorides, etc.

*These preparations were presented to us by A. F. Zhigach.

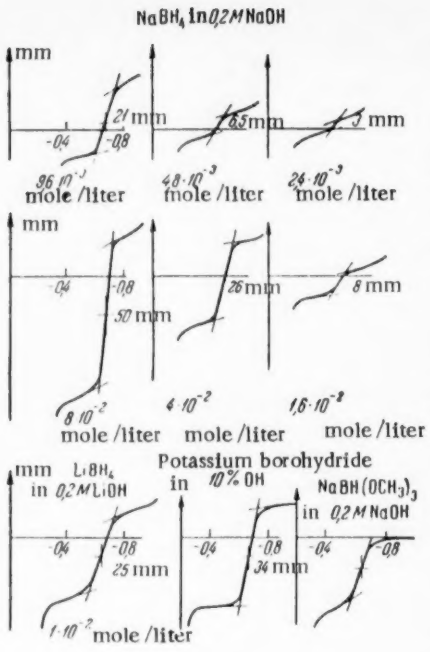

Fig. 1.

Thus, there can be no doubt that this wave is due to BH_4^- ions and that these ions produce no other wave.

These results refute the data of Pecsok. Of the properties of the borohydride wave, we first of all studied the dependence of the height of the wave on the concentration of BH_4^- ions. In the concentration range investigated, 10^{-3} to 10^{-1} mole/liter, this dependence is linear. The absence of a proportionality between the current and the square root of the effective pressure on the dropping mercury indicates that the limiting current is not completely diffusional.

The metal borohydrides in aqueous solution, especially in acid solution, decompose rapidly; consequently, it is extremely difficult to carry out polarography under these conditions. It was for precisely this reason that we prepared our solutions using the corresponding base and alkaline borate buffer mixtures, which simultaneously served as the supporting electrolyte. During the course of selecting the most convenient pH region for the work, we made a very important observation. It was observed that the height of the borohydride wave is strongly dependent on the pH of the medium for a given concentration. It changed in a regular manner, inversely, with a change in pH. When the pH of the solutions was sufficiently high (above 12.5), under which conditions the borohydrides are comparatively stable, there is practically no wave. Whence, it logically follows that the observed wave actually belongs not to the BH_4^- ion, but to some of the products of its hydrolysis. A series of investigations has established that hydrolysis of borohydrides proceeds in several stages, in one of which diborane is liberated under certain conditions [9-11]. The latter, like tetraborane, is capable of reacting with bases, forming the so-called hypoborates.

The work of V. I. Mikheeva and V. Yu. Surs [13] has shown experimentally that hypoborates can be considered as products of individual stages in the hydrolysis of borohydrides in accordance with the scheme

$$[BH_4]^- \rightarrow [BH_3(OH)]^- \rightarrow [BH_2(OH)_2]^- \rightarrow [BH_2(OH)_3]^- \rightarrow [B(OH)_4]^-$$

or $BO_2^- \cdot 2H_2O$.

TABLE 1

pH	$E_{1/2}$	tg α
$NaBH_4$, $4{,}8\cdot10^{-3}$ mole/liter		
9,24	−0,636	0,073
9,36	−0,649	0,088
9,50	−0,644	0,077
9,68	−0,658	0,063
9,97	−0,644	0,074
11,07	−0,652	0,065
0,17–0,2 *N* NaOH	−0,658	0,068
	−0,650	0,066
KBH_4, $5{,}7\cdot10^{-3}$ mole/liter		
10,82	−0,672	0,056
$LiBH_4$, $1\cdot10^{-1}$ моль/л		
Aqueous solution after heating to 70°	−0,65	0,063
Potassium hypoborate $1{,}5\cdot10^{-3}$ mole/liter		
10% KOH	−0,664	0,083
$NaBH(OCH_3)_3$ $1{,}77\cdot10^{-2}$ mole/liter		
0,2 *M* NaOH	−0,655	0,059

J. Goubeau and H. Kallfass [14], who studied this problem by means of infrared spectroscopy, did not observe any bands which could be assigned to $BH_2(OH)_2^-$ or $BH(OH)_3^-$ ions, but this does not contradict the reaction presented above, because, as noted by these authors, the failure to observe intermediate products was probably due to their high reactivity.

We passed gaseous diborane into cooled, concentrated solutions of KOH, NaOH, and LiOH.* The resulting solutions of hypoborates were polarographed, and the same wave with $E_{1/2} = -0.6$ v was obtained. Dilution of these solutions led, as in the case of the borohydride solutions, to a proportional decrease in the height of the wave. When the solutions were allowed to stand, the height of the "hypoborate" wave decreased with time, as did the height of the "borohydride" waves, and the decrease was in accordance with first order kinetics (with respect to hypoborate and borohydride, respectively) [8]. The wave practically disappeared when the solutions were boiled and also when they were strongly acidified, owing to decomposition of the hypoborates.

On the basis of these data, it must be concluded that the "borohydride" wave is in fact a "hypoborate" wave.

*The diborane was prepared by O. I. Rusetskii by means of electrical discharge.

The question as to which of the three hypoborates formed during hydrolysis corresponds to the polarographic wave is very difficult to answer, since it is apparently impossible to obtain for the experiments solutions of each of the hypoborates without the presence of the remaining hypoborates as impurities. Nevertheless, one may bring the following considerations to bear on the problem.

Kh. V. Shifrin and A. S. Bogonostsev of our laboratory studied the potassium iodate titration of solutions of borohydrides and of hypoborates during the course of hydrolysis at room temperature and during heating. It was found that freshly prepared solutions of lithium borohydride and lithium hypoborate, which, according to references [11 and 13], should contain only the first hydrolysis product, $LiBH_3(OH)$, are titrated by iodate, but they give no polarographic wave. Consequently, the wave cannot be ascribed to the $BH_3(OH)^-$ ion. When these solutions were heated to 60° and above, the wave appeared, and upon further heating of the solutions, the wave was retained as long as the solutions remained titratable. Since the last titratable hydrolysis product is the $BH(OH)_3^-$ ion, it must be responsible for the polarographic wave. This was confirmed by our experiments with sodium trimethoxyborohydride, $NaBH(OCH_3)_3$*, the anion of which like the $BH(OH)_3^-$ ion, contains only one active hydrogen (directly bonded to the boron), and this compound gave the same wave with $E_{1/2} = -0.65$ v (Table 1).

Contrary to Pecsok the electrode reaction responsible for the observed polarographic wave evidently cannot involve oxidation of BH_4^- ions with the participation of eight electrons, but must consist of oxidation of hypoborate ions, for example, in accordance with the equation: $BH(OH)_3^- + OH^- \rightarrow BO_2^- + 2H_2O + H + \bar{e}$ or, $BH(OH)_3^- + 2OH \rightarrow BO_2^- \cdot 2H_2O + H_2O + 2\bar{e}$.

The first of these reactions is in agreement with the value of the slope of the graphs of $i/(i_d - i) = f(E)$ for borohydrides and hypoborates, which is close to 0.059 (Table 1), which is characteristic of reactions involving one electron. The stoichiometric data, obtained in our laboratory on the iodatometric titration of $NaBH(OCH_3)_3$ support the first scheme.

The kinetics studied by Pecsok who used a polarographic method, in reality relate not to reactions of sodium borohydride, but to hydrolysis and oxidation of the intermediate products. In this case, the results of the investigation cannot be considered reliable, since they were obtained without taking into account the catalytic effect of mercury, which is very significant according to our data.

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*This compound was kindly presented to us by V. I. Mikheeva and T. N. Dymova.

cis- AND trans-1-HALOBUTADIENES AND THEIR BEHAVIOR IN THE DIENE SYNTHESIS

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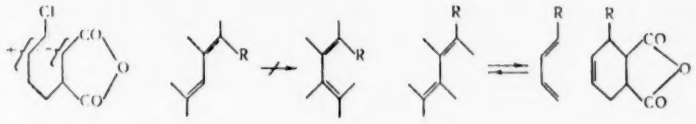
It has been reported in a number of papers [1-4] that 1-chloro-1,3-butadiene does not enter into the diene [Diels-Alder] synthesis. This behavior has been explained by the stabilizing effect of the chlorine atom at C_1 of the intermediate carbonium system (I), which, therefore, cannot undergo ring closure [5].



(I) (II) (IIa) (III) (IIIa) (IV)

However, the ability of 1-substituted butadienes to undergo diene synthesis reactions depends on their geometrical isomerism. It is know that cis isomers (II, R = CH_3, C_6H_5, CN, etc.), the structure of which hinders their conversion to the cisoid conformation (IIa), do not enter into this addition reaction, while trans-dienes (III), for which conversion into the cisoid conformation (IIIa) required for diene synthesis occurs readily, form the normal adducts in good yields [6-11]. From the fact that 1-chloro-2-methyl [12, 13], 1-chloro-3-methyl- [14], and 1,4-dichlorobutadienes [15] readily react with maleic anhydride, the conclusion follows that these dienes are the trans isomers. Up to the present, nothing has been known concerning the geometrical isomerism of 1-halobutadienes, and it could only be assumed that their trans isomers (III, R = Cl, Br) would enter into diene synthesis reactions, and the cis isomers (II, R = Cl, Br) would be inactive in this reaction.

We have now established that the 1-chlorobutadiene prepared by dehydrochlorination of 1,4-dichloro-2-butene [2, 3, 16] is a mixture of the cis and trans isomers in a ratio of approximately 9:1, which cannot be separated in a column of 25 theoretical plates. When this mixture was reacted with maleic anhydride (50-55°, 12 hours), the normal diene synthesis product was formed in 10% yield; the structure of this product was proved by dehydrogenation to phthalic anhydride. Without doubt, this fact shows that the initial mixture contained about 10% trans-1-chlorobutadiene, which formed the adduct.

In conformity with its configuration, the cis isomer remaining after separation of the adduct was actually incapable of taking part in the diene synthesis. However, cis-1-chlorobutadiene is comparatively easily converted to the trans isomer in the presence of iodine, yielding an equilibrium mixture of the cis and trans forms as in the case of cis-piperylene [17]. As a result, when a mixture of cis-1-chlorobutadiene and maleic anhydride is heated in the presence of iodine, an adduct of the trans isomer is gradually formed, and the yield can reach 80%. This conversion of cis-1-chlorobutadiene to the trans form also takes place at room temperature; however, the reaction rate is low. Raman spectra have been obtained for the cis isomer and a mixture of the cis and trans isomers of 1-chloro-1,3-butadiene [18]. Similarly, 1-bromo-1,3-butadiene prepared by dehydrobromination of 1,4-dibromo-2-butene [3, 19] is a mixture of cis and trans isomers (II + III, R = Br) in a ratio of approximately 14:1, as was shown by condensation of the trans isomer with maleic anhydride and separation of the cis isomer.

Cis-1-bromobutadiene also isomerizes to the trans form in the presence of iodine; the trans form then reacts with maleic anhydride to form an adduct which, under the experimental conditions employed (~70°, 100 hours), splits out hydrogen bromide and adds another molecule of maleic anhydride to give a bisanhydride having the composition $C_{12}H_8O_6$.

EXPERIMENTAL

The 1-chloro-1,3-butadiene (II + III, R = Cl) was prepared from 1,4-dichlorobutene and had the following constants: b. p. 66-67° at 760 mm; n_D^{20} 1.4712; d_4^{20} 0.9537. MR: found, 25.93; calculated for C_4H_5Cl, F_2, 24.61. λ = 232, ϵ = 17400.

3-Chloro-Δ^4-cyclohexene-1,2-dicarboxylic anhydride (IV, R = Cl). A mixture of 88.5 g (1 mole) of 1-chlorobutadiene and 33 g (0.3 mole) of maleic anhydride (plus hydroquinone) was allowed to stand at room temperature overnight, and the mixture was then heated at 50-55° for 12 hours. The precipitated crystalline reaction product was filtered, and 18.3 g (~10%) of anhydride (IV) was obtained. After recrystallization from a mixture of benzene and acetone, the anhydride had an m. p. of 130-131°.

Found %: C 51.42; H 3.78; Cl 19.24. Calculated % for $C_8H_7O_3Cl$: C 51.48; H 3.78; Cl 19.01.

Fusion of the adduct with sulfur (~230°) until hydrogen sulfide was no longer evolved led to the formation of phthalic anhydride with an m. p. of 130-131°, which was identical to the m. p. of a known sample.

cis-1-Chloro-1,3-butadiene (II, R = Cl). To the diene remaining after separation of the adduct was added 5 g of maleic anhydride, and the solution was heated at 50-55° for an additional 12 hours. There was no detectable further formation of adduct. The unreacted cis-1-chlorobutadiene was distilled in a column of 25 theoretical plates. There was obtained 68 g (~78%) of pure cis-diene (II); b. p. 66.8-67°; n_D^{20} 1.4703; d_4^{20} 0.9553. MR: found, 25.86; calculated for C_4H_5Cl, F_2, 24.61. λ = 232, ϵ = 17400.

Found %: C 54.31; H 5.74; Cl 40.05. Calculated % for C_4H_5Cl: C 54.26; H 5.70; Cl 40.05.

Isomerization of cis-1-chlorobutadiene (II) to trans isomer (III). A mixture of 50 g of the pure cis isomer, 1 g of iodine, and 50 ml of dry toluene was heated in an ampoule at 100° for 20 hours. After removal of the iodine with sodium hypochlorite, the mixture of isomers was distilled in a column of 25 theoretical plates:

	B. p., °C	Amt., g	n_D^{20}	d_4^{20}
1st Fraction	66,8—67	20,0	1,4703	—
2nd Fraction	67,0—67,2	7,5	1,4720	0,9608
3rd Fraction	67,2—67,5	4,2	1,4724	0,9608
4th Fraction	67,5	2,4	1,4724	0,9608

To 5 ml of dry toluene was added 3.7 g of Diene Fraction 3 and 1 g of maleic anhydride (plus hydroquinone), and the mixture was heated in an ampoule at 60° for 6 hours. There was obtained 0.7 g of crystalline adduct (IV), which was identical with that described above with an m. p. of 130°

Condensation of a mixture of cis- and trans-1-chlorobutadienes with maleic anhydride in the presence of iodine.

a) To a solution of 3.7 g of the original mixture of 1-chlorobutadiene isomers and 4 g of maleic anhydride in 20 ml of benzene was added 2% iodine and a small amount of hydroquinone, and the mixture was heated in an ampoule on a boiling water bath for 24 hours. There was obtained 5 g of adduct (IV) with an m. p. of 130°.

b) To 10 ml of dry benzene were added 1.7 g (0.02 mole) of 1-chlorobutadiene, 1.9 g (0.02 mole) of maleic anhydride, 2% iodine, and a trace of hydroquinone, and the mixture was allowed to stand in a sealed ampoule at room temperature for 6 months. The precipitated crystalline adduct was separated, and 2.8 g (80%) of the adduct (IV) described above was obtained; m. p. 130.5°.

1-Bromo-1,3-butadiene (II + III, R = − Br) was prepared from 1,4-dibromo-2-butene (m. p. 53°) and had the following constants: b. p. 47-48.2° at 161 mm, n_D^{20} 1.5112, d_4^{20} 1.3777. MR_D: found, 28.78; calculated for C_4H_5Br, F_2, 27.5.

3-Bromo-Δ^4-cyclohexene-1,2-dicarboxylic anhydride (IV, R = Br). A mixture of 56 g of the original 1-bromobutadiene (II + III) and 5 g of maleic anhydride was allowed to stand in the presence of iodine at 25-30° for 5 days. The precipitated crystalline reaction product was separated, and 7 g (~7%) of adduct (IV) was obtained; m. p. 107-109° with decomposition (from benzene).

Found %: C 41.62; H 3.09; Br 34.16. Calculated % for $C_8H_7O_3Br$: C 41.58; H 3.05; Br 34.16.

Fusion of this adduct with sulfur at 230-235° until hydrogen sulfide was no longer evolved gave phthalic anhydride with an m. p. of 130°; this material did not depress the melting point of a known sample.

cis-1-Bromo-1,3-butadiene (II, R = Br). The liquid mixture remaining after separation of the adduct was distilled in a flask fitted with a dephlegmator, and, after a second distillation over sodium, pure cis-1-bromo-1,3-butadiene (II) was obtained with b. p. of 47-48° at 161 mm; n_D^{20} 1.5100; d_4^{20} 1.3878. MR_D: found 28.68; calculated for C_4H_5Br, F, 27.50.

Found %: C 36.32; H 3.84; Br 59.36. Calculated % for C_4H_5Br: C 36.12; H 3.78; Br 60.09.

Condensation of a mixture of cis- and trans-1-bromobutadienes with maleic anhydride in the presence of iodine. A mixture of 22 g (0.17 mole) of the original 1-bromobutadiene, 18.6 g (0.17 mole) of maleic anhydride, and 0.4 g of iodine in 50 ml of dry benzene was heated in a sealed ampoule at 70° for 100 hours. This gave 8.3 g of (crude) crystalline product; the yield was 37%. The substance was soluble in acetone and acetic anhydride, and was a bisanhydride having the composition $C_{12}H_8O_6$; m. p., 364°.

Found %: C 58.20; H 3.46. Calculated % for $C_{12}H_8O_6$: C 58.07; H 3.25.

The substance underwent alkaline hydrolysis like the anhydride of a tetrabasic acid.

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*Original Russian pagination. See C. B. translation.

NEW ESTERS OF DITHIOCARBAMIC ACIDS

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In connection with the appearance in the literature of data relating to the protection from ionizing radiation afforded by β-aminoethylisothiuronium bromide (I) (AET, an antirad) [1, 2], it seemed of interest to synthesize compounds with related structures, namely, β-aminoethyldithiocarbamates (II).

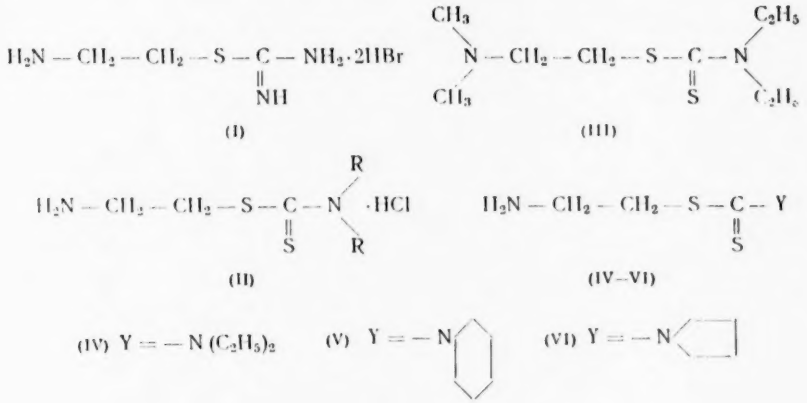


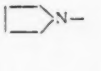
TABLE 1

β-Aminoethyldithiocarbamates

Subs. No.	Y	Substance (as hydrochloride)	Crystallization solvent	M. p., °C	Yield, %	Molecular formula	N, % found	N, % calc.	S, % found	S, % calc.
IV	C_2H_5, C_2H_5 N–	β-Aminoethyl diethyldithiocarbamate	Ethyl acetate	122–124	61	$C_7H_{16}N_2S_2 \cdot HCl$	12,50	12,25	27,91	28,08
V	N–	β-Aminoethyl pentamethylenedithiocarbamate	Ethyl acetate + alcohol	187–189	59	$C_8H_{16}N_2S_2 \cdot HCl$	11,15	11,43	26,40	26,66
VI	N–	β-Aminoethyl tetramethylenedithiocarbamate	Alcohol	184–186	60	$C_7H_{14}N_2S_2 \cdot HCl$	12,13	12,36	28,10	28,25

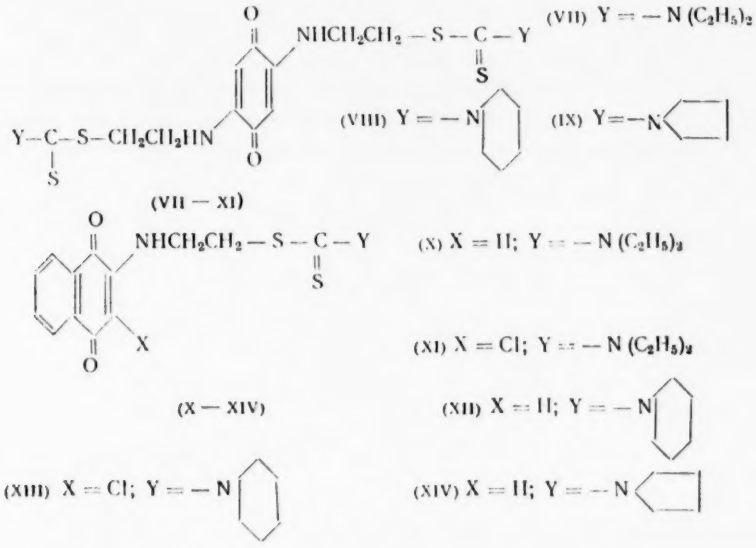
TABLE 2

Products of the Interaction of β-Aminoethyl Dithiocarbamates with Quinones

Subs. No.	X	Y	Substance name	Form of crystals under microscope	Crystallization solvent	M. p., °C	Yield, %	Molecular formula	N, %		S, %	
									found	calc.	found	calc.
VII	H	$(C_2H_5)_2N-$	2,5-bis[β-(diethyldithiocarbamino)ethylamino]benzoquinone	Fine, red	Dimethylformamide	182-184	52	$C_{20}H_{32}O_2N_4S_4$	11.44	11.47	26.05	26.25
VIII	H		2,5-bis[β-(pentamethylenedithiocarbamino)ethylamino]-benzoquinone	Very fine, red	Dimethylformamide	223-225	51	$C_{22}H_{32}O_2N_4S_4$	10.99	10.95	25.03	25.00
IX	H		2,5-bis[β-(tetramethylene-dithiocarbamino)ethylamino]-benzoquinone	Very fine, brick red	Dimethylformamide	226-228	53	$C_{20}H_{28}O_2N_4S_4$	11.18	11.51	26.40	26.44
X	H	$(C_2H_5)_2N-$	2-[β-(diethyldithiocarbamino)ethylamino]-1,4-naphthoquinone	Orange-red	Dimethylformamide	113-115	59	$C_{17}H_{20}O_2N_2S_2$	8.19	8.04	18.80	18.39
XI	Cl	$(C_2H_5)_2N-$	2-[β-(diethyldithiocarbamino)ethylamino]-3-chloro-1,4-naphthoquinone	Red	Ethyl alcohol	135-137	57	$C_{17}H_{19}O_2N_2S_2Cl$	6.96	7.32	16.96	16.73
XII	H		2-[β-(pentamethylenedithiocarbamino)ethylamino]-1,4-naphthoquinone	Red	Dimethylformamide	176-177	51	$C_{18}H_{20}O_2N_2S_2$	7.79	7.78	18.02	17.77
XIII	Cl		2-[β-(pentamethylenedithiocarbamino)ethylamino]-3-chloro-1,4-naphthoquinone	Red	Dimethylformamide	172-173	50	$C_{17}H_{18}O_2N_2S_2$	7.84	8.09	18.89	18.50
XIV	H		2-[β-(tetramethylenedithiocarbamino)ethylamino]-1,4-naphthoquinone	Orange	Dimethylformamide	144-146	53	$C_{18}H_{19}O_2N_2S_2Cl$	7.12	7.10	16.90	16.22

Only one compound of this structure – β-dimethylaminoethyl diethyldithiocarbamate (III) – is described in the literature [3]. We have now prepared new carbamates with an unsubstituted amino group (IV, V, and VI). These substances were prepared by the interaction of β-chloroethylamine and the sodium salts of the corresponding dithiocarbamic acids (sodium diethyldithiocarbamate, sodium tetramethylenedithiocarbamate, and sodium pentamethylenedithiocarbamate). These substances were isolated in the form of the readily crystallizable hydrochlorides (Table 1).

Through the use of the well-known reaction of amines with quinones, we accomplished the synthesis of new derivatives of benzoquinone and naphthoquinone (VII-XIV).



Interest in such compounds arises from the fact that new physiologically active quinones have recently become known [4-6], as have new synthetic medicinal preparations containing a quinone nucleus (for example, antibacterial substances [7] and ethylenimine derivatives with anti-tumor properties [7, 8]).

The formation of benzoquinone (VII-IX) and naphthoquinone (X-XIV) derivatives containing β-aminoethyldithiocarbamate radicals takes place smoothly upon interaction of the free amines (IV, V, and VI) and the quinone in ether solution; the compounds are readily crystallizable, difficultly soluble, red substances (Table 2).

TABLE 3

Carboxymethyl Dithiocarbamates (Y–C(=S)–S–CH_2COOH)

Y	Substance	M. p., °C	Yield, %	Molecular formula	N, % found	N, % calc.	S, % found	S, % calc.
$(C_2H_5)_2N$–	Carboxymethyl diethyldithiocarbamate	82–84	82	$C_7H_{13}O_2NS_2$	7,05	6,76	31,60	30,91
N–	Carboxymethyl pentamethylenedithiocarbamate	139–141	81	$C_8H_{13}O_2NS_2$	6,69	6,39	29,60	29,22
N–	Carboxymethyl tetramethylenedithiocarbamate	141–143	83	$C_7H_{11}O_2NS_2$	7,14	6,83	30,82	31,27

EXPERIMENTAL

Preparation of the dithiocarbamates. The sodium pentamethylene- and tetramethylenedithiocarbamates were prepared by the interaction of the corresponding amines (piperidine and pyrrolidine) with hydrogen sulfide in benzene solution in the presence of sodium hydroxide. The dithiocarbamates were converted to the carboxymethyl derivatives for characterization, and these were prepared by the interaction of the sodium salts of the dithiocarbamic acids with monochloroacetic acid. The carboxymethyl derivatives crystallizize readily from water, and are colorless products with comparatively low melting points (Table 3).

β-Aminoethyl dithiocarbamates. A solution was prepared by dissolving 0.01 mole of the respective sodium dithiocarbamate in the minimum amount of cold water. Another solution was prepared by dissolving 0.01 mole of β-chloroethylamine hydrochloride in a small amount of water, and the solution was made alkaline by adding sodium hydroxide until the solution was strongly alkaline. The two solutions were combined, and the reaction mixture was allowed to stand for a day at room temperature. An oil separated, and it was extracted with ether. The dried ether extract was saturated with dry hydrogen chloride, whereupon the β-aminoethyl dithiocarbamate hydrochloride precipitated. This was filtered and washed with ether.

Reaction of the aminoethyl dithiocarbamates with quinones. To an ether solution of the quinone (0.01 mole) was added an ether solution of the β-aminoethyl ester of the respective dithiocarbamic acid in an amount of 0.01 mole in the case of naphthoquinone and 0.02 mole in the case of benzoquinone. The solutions were allowed to stand, whereupon lustrous red-orange crystals precipitated.

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THE REACTION OF DIALKYL PHOSPHITES WITH QUINONES

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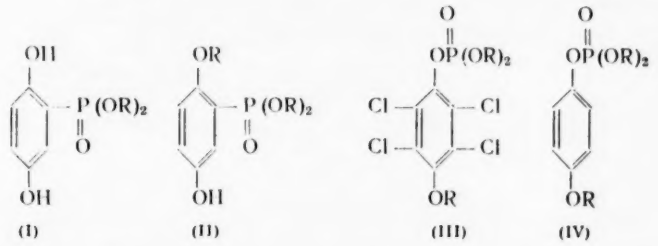
Our earlier work [1-3] has shown that organophosphorus compounds are excellent lubricating oil additives. Such compounds include, for example, certain derivatives of dithiophosphoric, phosphoric, and phosphorous acids. It appeared to be of considerable interest to prepare organophosphorus compounds which, in addition to other properties, would also have antioxidant properties, i.e., additives inhibiting oxidation of hydrocarbons by atmospheric oxygen.

We decided to attempt to carry out the addition of partial esters of phosphorous acid, dialkyl phosphites, to quinone. This reaction is important of itself. V. S. Abramov [4, 5] investigated the interaction of dialkyl phosphites with aldehydes and quinones in the presence of an alcoholate. This work established that the dialkyl phosphites are added at the carbonyl group with the formation of α-hydroxyalkanephosphonic acids. A. N. Pudovik, Yu. P. Kitaev, and G. Z. Zamataeva [6-8] carried out the addition of dialkyl phosphites to various unsaturated compounds; these reactions were also carried out in the presence of alcoholates. In this case, the addition to unsaturated ketones occurred at the carbon–carbon double bond.

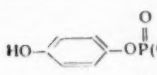
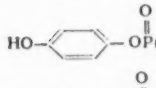
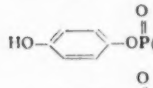
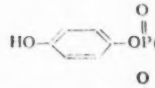
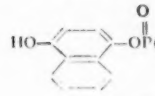
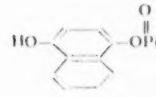
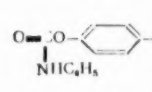
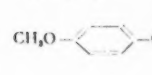
In the case which we have considered, the interaction of dialkyl phosphites with p-benzoquinone would presumably lead to the formation of esters of dihydroxyphenylphosphonic acids (I). The possibility that the



(I) (II) (III) (IV)

reaction would proceed in this direction may be inferred from the data in the patent to Ladd and Harvey [9]. The addition of complete esters of phosphorous acid to p-benzoquinone was accomplished in some recently published work [10], in which it was shown that the reaction leads to compounds of the type of (II). Moreover, there are indications in the literature that the addition of phosphites to p-benzoquinone and certain of its derivatives can also occur in another direction, namely, with the formation of compounds in which the phosphorus is bonded to oxygen. Thus, in the work reported in reference [11], the interaction of triethyl phosphite with chloranil gave as the major reaction product a compound with the structure (III). The authors of reference [12] assigned a structure analogous to (IV) to compounds obtained as a result of the reaction of trialkyl phosphites with p-benzoquinone. Subsequent work [13, 14] confirmed their conclusion.

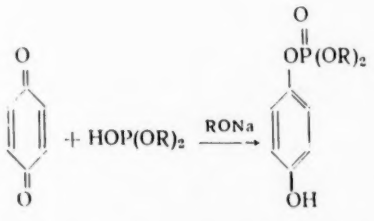
TABLE 1

Phosphoric acid ester	M. p., °C	C, % found	C, % calc.	H, % found	H, % calc.	P, % found	P, % calc.	OH, % found	OH, % calc.	Yield, %
	74,5—75,5	43,87 43,75	44,10	5,17 5,07	5,05	14,04 14,28	14,26	7,76 7,89	7,80	70
	38,0—39,0	49,06 48,99	48,80	6,15 6,06	6,09	12,66 12,69	12,60	—	—	41
	49,0—50,0	52,41	52,55	7,07	6,93	11,31	11,40	6,22	6,13	53
	52,5—53,5	55,32 55,44	55,62	7,81 7,82	7,61	10,24 10,31	10,26	5,57 5,21	5,59	50
	154,5	—	—	—	—	11,57	11,40	—	—	62
	93,0—95,0	—	—	—	—	9,30	9,06	—	—	—
	141,0	—	—	—	—	11,47	11,55	—	—	62
	98,5—99,0	—	—	—	—	10,60	10,45	—	—	51
	120,0—121,0	53,37 53,45	53,40	4,77 4,79	4,68	9,16 9,19	9,20	—	—	89
	B. p., 153,0—156,0° (3 мм)**	—	—	—	—	13,62	13,37	—	—	42,4

*Nitrogen content, in %: found, 4.25, 4.35; calculated, 4.15.

**n_D^{20} 1.4968; d_{20}^{20} 1.2511.

We have now established that the interaction of dialkyl phosphites with p-benzoquinone forms dialkyl p-hydroxyphenyl phosphates; consequently, the phosphorus containing group added to the oxygen atom of the benzoquinone according to the equation:

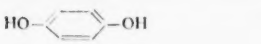
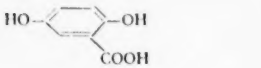
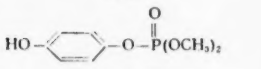
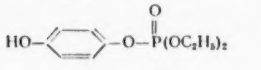
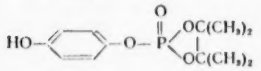
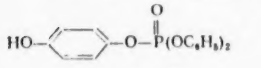
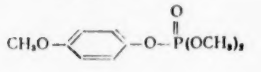


The addition was accompanied by the usual conversion of the quinoid structure of the ring to a benzene structure. The interaction of dialkyl phosphites with α-naphthoquinone proceeded along a similar route. Table 1 presents the melting points and the analytical results obtained for these compounds.

The reactions were carried out with equimolar amounts of p-benzoquinone (or α-naphthoquinone) and dialkylphosphite in the presence of sodium alcoholate. The solvent was a dry alcohol containing the same hydrocarbon radical as in the alkoxy group of the phosphite; benzene was also used as a solvent. Dioxane and diethyl ether were used as solvents during the interaction of the tetramethylethylene glycol ester of phosphorous acid and of diphenyl phosphite with p-benzoquinone. The reaction yielded crystalline substances, which were soluble in aqueous solutions of bases and which gave the characteristic color reaction for a phenol group with ferric chloride; the compounds did not undergo reactions characteristic of carbonyl groups.

TABLE 2

U. V. Absorption Spectra of Hydroquinone Derivatives

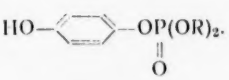
Compound	λ_{max}, mμ	log ε
	290	3,4
	320	—
	280	3,7
	280	3,67
	280	3,69
	280	3,66
	280	3,69

Hydrolysis of these compounds with hydrochloric acid (1 : 1) gave a hydroquinone in a yield of up to 80%. Saponification with alcoholic alkali at 40-50° also led to the formation of a hydroquinone (corresponding to the phenolate) and a phosphorus compound. Quantitative determination of the hydroxyl group content by acetylation with acetic anhydride in the presence of pyridine showed that each of the compounds prepared had only one hydroxyl group. For one compound, namely, the one prepared from dimethyl phosphite and p-benzoquinone, a reaction was carried out with phenyl isocyanate, and the corresponding phenylurethan was isolated.

A study of the ultraviolet absorption spectra of these compounds also confirmed that the compounds were p-hydroxyphenyl mixed esters of phosphoric acid. Indeed, had the products of the reaction of dialkyl phosphites with quinones been esters of hydroquinonephosphonic acid (I), the spectra should have shown a shift of the absorption maxima toward the longer wave lengths, as compared to hydroquinone, as occurs in the case of 2,5-dihydroxybenzoic acid [15] and nitrohydroquinone [16], for example. On the other hand, if the structure of these compounds were that of a p-hydroxyphenol phosphate (IV), it would be expected that the maxima would shift toward the shorter wave lengths, as in the case of O-acetyl derivatives of hydroquinone [17].

As may be seen upon examination of Table 2, the maxima of the products of the interaction of dialkyl phosphites with quinones shifted toward the shorter wave lengths, and coincided with the absorption maximum of dimethyl p-methoxyphenyl phosphate. The latter compound was synthesized by a known method [18], and there was no reason to doubt its structure.

Thus, the results of our investigation of the substances obtained by the interaction of dialkyl phosphites with p-benzoquinone (hydrolysis with the formation of hydroquinone, the absence of carbonyl groups, the presence of a single phenolic hydroxyl) show that these substances are indeed esters of phosphoric acid, i.e., dialkyl p-hydroxyphenyl phosphates:



EXPERIMENTAL

Dimethyl p-hydroxyphenyl phosphate. To a solution of 5.5 g (0.05 mole) of dimethyl phosphite in 40 ml of dry methyl alcohol was added about 1 ml of a solution of sodium methylate, and, after the resulting solution had been cooled to 0°, 5.4 g (0.05 mole) of benzoquinone was added in small portions. The reaction mixture was then heated for an hour and a half on a water bath. Upon completion of the reaction, the methyl alcohol was distilled, whereupon the residue crystallized. Two recrystallizations from water yielded 7.3 g (70.7% of theoretical) of the ester; m. p. 74.5-75.5°.

Ester of phenylcarbamic acid (a phenylurethan). A mixture of 2.1 g of dimethyl p-hydroxyphenyl phosphate and 4 ml of phenyl isocyanate was heated at 75-85° for 10 hours on a water bath. The resulting white, crystalline substance was washed with petroleum ether and then twice recrystallized from benzene; m. p. 120-121°

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*Original Russian pagination. See C. B. translation.

THE INTERACTION OF SILICON HYDRIDES WITH ACRYLONITRILE IN THE PRESENCE OF IRON PENTACARBONYL AND NICKEL CHLORIDE

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As we have shown in earlier work [1], silicon hydrides interact with unsaturated compounds in the presence of iron pentacarbonyl with the formation of saturated and unsaturated compounds in accordance with schemes (A) and (B):

$$R'R''R'''SiH + CH_2=CHR \rightarrow R'R''R'''SiCH_2CH_2R; \quad (A)$$

$$R'R''R'''SiH + CH_2=CHR \rightarrow R'R''R'''SiCH=CHR, \quad (B)$$

where R', and R'' are, respectively, alkyl, chlorine, and an ethoxy group; R is an alkyl group or OC_2H_5. Which of these reactions will predominate will depend on the natures of the silane and olefin and also on the reaction conditions.

In the present work, we investigated the reaction between silicon hydrides and acrylonitrile in the presence of iron pentacarbonyl. Since 1956, a considerable amount of work has been devoted to the reaction of silicon hydrides with acrylonitrile [2-11]. Organic bases, acid amides, platinum on carbon, chloroplatinic acid, and Raney nickel have been used as catalysts for this reaction. Peroxides cannot be used in this reaction, since they cause polymerization of the acrylonitrile [3].

Organic bases and amides catalyze only the reaction of trichlorosilane with acrylonitrile, and they are inactive for the reaction of methyldichlorosilane with acrylonitrile [5-7]. Methyldichlorosilane reacts with acrylonitrile in the presence of platinum catalysts and Raney nickel; however, a mixture of α- and β-methyldichlorosilylpropionitriles is formed.

Nozakura and Konotsune [2] showed that cyanethylation of trichlorosilane takes different directions under the influence of different catalysts. Thus, β-trichlorosilylpropionitrile is formed when the reaction is carried out in glass tubes in the presence of catalytic amounts of pyridine. Under the same conditions but in an autoclave, α-trichlorosilylpropionitrile is formed. This is due to the formation of tetrapyridinenickel chloride in the autoclave (owing to the reaction of the trichlorosilane with the metal walls of the autoclave). Thus, since cyanethylation of trichlorosilane can be directed either toward the formation of β-trichlorosilylpropionitrile or toward the formation of the α-isomer, a mixture of the α- and β-isomers were formed in the cyanethylation of methyldichlorosilane under all of the conditions studied up to the present time.

we have studied the interaction of methyldichlorosilane and of triethylsilane with acrylonitrile. The reaction was carried out in a stainless steel autoclave or in selaed glass ampoules at 120-150° in the absence and in the presence of iron pentacarbonyl, nickel chloride, and a mixture of the two promoters; the results obtained are shown in Table 1. As may be seen from the data of Table 1, the reaction did not go in the absence of a

promoter (Experiment 6), nor did a reaction occur in the presence of nickel chloride alone (Experiments 7 and 10). Triethylsilane did not react with acrylonitrile in the presence of iron pentacarbonyl in the autoclave (Experiment 13). Methyldichlorosilane did not react with acrylonitrile in the presence of iron pentacarbonyl in a sealed glass ampoule (Experiment 9), but when the experiments were carried out in the autoclave under the same conditions, an addition product was formed, the yield of which increased with an increase in the excess acrylonitrile (Experiments 1-5). These data suggest that reaction occurs when there are present in the reaction mixture, in addition to the iron pentacarbonyl, traces of heavy metal salts formed on the autoclave walls under the action of the chlorosilanes.

TABLE 1

Expt. No.	Silane	Mole ratio silane : nitrile	Reaction vessel	Promoter	Temp., °C	Yield, % of theoretical
1	CH_3SiCl_2H	2 : 1	Stainless steel autoclave*	$Fe(CO)_5$ (1 ml)	140—150	0
2	The same	1 : 1	The same	$Fe(CO)_5$ (1 ml)	140—150	12
3	The same	1 : 2	The same	$Fe(CO)_5$ (1 ml)	140—150	39
4	The same	1 : 3	The same	$Fe(CO)_5$ (1 ml)	140—150	46
5	The same	1 : 5	The same	$Fe(CO)_5$ (1 ml)	140—150	42
6	The same	1 : 3	The same	No promoter	140—150	0
7	The same	1 : 3	The same	$NiCl_2$ (0.15 g)	140—150	0
8	The same	1 : 3	The same	$Fe(CO)_5$ (1 ml)	120—130	60
9	The same	1 : 3	Sealed glass ampoule**	$NiCl_2$ (0.15 g) + + $Fe(CO)_5$ (0.2 g)	140—150	0
10	The same	1 : 3	The same	$NiCl_2$ (0.1 g)	140—150	0
11	The same	1 : 3	The same	$Fe(CO)_5$ (0.2 ml) $NiCl_2$ (0.1 g)	120—130	56
12	$(C_2H_5)_3SiH$	1 : 3	Stainless steel autoclave*	$Fe(CO)_5$ (1 ml) + + $NiCl_2$ (0.15 g)	120—130	73
13	The same	1 : 3	The same	$Fe(CO)_5$ (1 ml)	140—150	30
14	CH_3SiCl_2H ***	2 : 1	The same	$Fe(CO)_5$ (1 ml)	140—150	4

*The experiments were carried out in a half-liter rotating autoclave; the charge to the autoclave amounted to 200-300 g of the mixture of silane and acrylonitrile. The air was purged from the autoclave with nitrogen, after which nitrogen was introduced into the autoclave to a pressure of 30 atm. The heating time was 5 hours in all experiments.

**The experiments were carried out with 17.2 g of the silane and 24.3 g of acrylonitrile. The heating time was 5 hours.

***The reaction was carried out in 150 ml of acetonitrile.

However, when small amounts of iron pentacarbonyl and nickel chloride were present, acrylonitrile added to both methyldichlorosilane and triethylsilane. The reactions proceeded equally well in the autoclave (Experiments 8 and 12), and in the sealed ampoules (Experiment 11). The addition leads to α-methyldichlorosilylpropionitrile ($CH_3SiCl_2CH(CH_3)CN$) in the case of methyldichlorosilane and to α-triethylsilylpropionitrile ($(C_2H_5)_3SiCH(CH_3)CN$) in the case of triethylsilane. Apparently, the action of this mixed catalyst which we discovered, causes the reaction to proceed by an ionic mechanism. The following reasons may be cited in support of this opinion: a) The reaction proceeds only in the presence of an excess of acrylonitrile (Experiments 4-5) or in a medium of another polar solvent, for example, acetonitrile (Experiment 14); b) the participation of nickel chloride is necessary; c) in the cyanethylation of silicon hydrides, the formation of α-isomers is usually associated with an ionic reaction mechanism [9].

EXPERIMENTAL

We shall present a description of Experiments 8 and 12 and the proof of structure of the addition products.

Reaction of methyldichlorosilane with acrylonitrile in the presence of $Fe(CO)_5$ and $NiCl_2$ (Experiment 8). To a half-liter stainless steel rotating autoclave were charged 115 g (1 mole) of CH_3SiCl_2H, 160 g (3 moles) of $CH_2=CH-CN$, 1 ml of $Fe(CO)_5$ and 0.15 g of $NiCl_2$. The air was purged from the autoclave with nitrogen, after which nitrogen was introduced to a pressure of 30 atm. The reaction mixture was heated for 5 hours at 120-130°, and was then fractionated under vacuum. There was obtained 102 g (60% of theoretical) of α-methyldichlorosilylpropionitrile (I) with a b. p. of 59-60° at 1 mm; n_D^{20} 1.4490; d_4^{20} 1.1635. MR: found, 38.74; calculated for $N_4H_7SiCl_2N$, 38.62. Found % Si: 17.21, 16.88. Calculated % Si: 16.71. Titration with 0.1 N NaOH gave 42.49 and 42.41% Cl. Calculated % Cl for $C_4H_7SiCl_2N$: 43.17.

Proof of the structure of the addition product was carried out by the known scheme [2, 4]:

$$CH_3SiCl_2CHCN \xrightarrow{0.1N\,NaOH} CH_3Si(O)_{1/2}-CHCN + 2HCl; \quad (1)$$

(I)

$$CH_3SiCl_2CHCN + 3CH_3MgI \rightarrow (CH_3)_3SiCHCN + C_2H_5CCH_3; \quad (2)$$

$$C_2H_5CCH_3 + NH_2NHC_6H_3(NO_2)_2 \rightarrow C_2H_5CCH_3 \quad (2')$$

$$\| O \qquad\qquad \| N-NHC_6H_3(NO_2)_2;$$

$$CH_2SiCl_2CHCN + 2CH_3MgI \rightarrow (CH_3)_3SiCHCN; \quad (3)$$

$$(CH_3)_3SiCHCN \xrightarrow{40\%KOH} (CH_3)_3SiOSi(CH_3)_3 + CH_3CH_2COOH; \quad (4)$$

(II)

$$CH_3CH_2COOH + NH_2NHC_6H_5 \rightarrow CH_3CH_2CONHNH \quad (4')$$

$$\qquad\qquad\qquad

Methylation with an excessof Grignard reagent gave, in addition to product (II), methyl ethyl ketone with a b. p. of 80-82° and n_D^{20} 1.3885. Literature values [12]: b. p. 79.6° and n_D^{20} 138071 [15,9].

The ketone was identified as the 2,4-dinitrophenylhydrazone, m. p., 115° (from alcohol). Found % N: 23.26 and 22.92. Calculated % N for $C_{10}H_{12}O_4N_4$: 22.21. Literature values [12]: m.p., 117°.

Alkaline hydrolysis of trimethylsilylpropionitrile. Substance (II) was refluxed for 7 hours with 45% KOH. The following substances were obtained: 1) $(CH_3)_3Si{-}O{-}Si(CH_3)_3$, b. p. 99°, n_D^{20} 1.3740; d_4^{20} 0.7656. MR: found, 48.42; calculated for $C_6H_{18}Si_2O$, 48.89. Literature values [13]: n_D^{20} 1.3792; d_4^{20} 0.7638.

Found %: C 44.43, 44.31; H 11.37, 11.51. Calculated % for $C_6H_{18}Si_2O$: C 44.38; H 11.17.

2) CH_3CH_2COOH with a b. p., of 141°, n_D^{20} 1.3871. Literature values [12]: b. p. 141°, n_D^{20} 1.3874. The acid was identified as the phenylhydrazide, m. p. 153-155° (from benzene). Found % N: 16.68 and 16.57. Calculated % N for $C_9H_{12}N_2O$: 17.06. Literature values [2]: M. p. 155-156°.

Reaction of triethylsilane with acrylonitrile in the presence of $Fe(CO)_5$ and $NiCl_2$ (Experiment 12). The experiment was carried out in the same manner as with methyldichlorosilane. From 87 g (0.75 mole) of triethylsilane, 132 g (2.5 mole) of acrylonitrile, 0.5 ml of $Fe(CO)_5$, and 0.2 g of $NiCl_2$ was obtained 92 g (73% of theoretical) of a substance with a b. p. of 97-98° at 8 mm. After a second distillation, the substance had n_D^{20} 1.4525; d_4^{20} 0.8634. MR: found, 52.95; calculated for $C_9H_{19}SiN$, 52.88.*

Found %: C 63.77, 63.49; H 11.38, 11.33; Si 16.83, 16.85. Calculated % for $C_9H_{19}SiN$: C 63.85; H 11.31; Si 16.57.

Alkaline hydrolysis, carried out similarly to that described above, gave hexaethyldisiloxane and propionic acid.

The infrared spectrum of this compound had a band at 2205 ± 10 cm^{-1}, which is characteristic of α-nitriles.

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* The calculation was carried out using the group contributions proposed by V. F. Mironov and G. I. Nikishin [14].

** Original Russian pagination. See C. B. translation.

SYNTHESIS AND REACTIONS OF TRIALKYLSILYLETHYNYLVINYL ALKYL ETHERS

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Syntheses based on diacetylene have opened up extensive possibilities of preparing a whole series of ethynylvinyl alkyl ethers, which are highly reactive. Various reactions involving ethynylvinyl alkyl ethers have been widely investigated in the work of Herberts [1], Franke [2], and other investigators [3-7] who have described the synthesis and reactions of these compounds with alcohols, ketones, and mercaptans. Diacetylene and monosubstituted diacetylenes form the corresponding magnesium bromide derivatives [8-10], and interaction of the latter with various carbonyl compounds and with carbon dioxide has been described in the literature [11]. We have previously studied the interaction of diacetylene with trialkylchlorosilanes through the reaction series [12]:

$$HC \equiv C - C \equiv CH \xrightarrow{C_2H_5MgBr} BrMgC \equiv C - C \equiv C - MgBr \xrightarrow{R_3SiCl} \rightarrow R_3SiC \equiv C - C \equiv C - SiR_3. \quad (1)$$

Dornow and Ische [13, 14] prepared the magnesium bromide derivatives of ethynylvinyl methyl and ethynylvinyl ethyl ethers, and condensed them with diethyl carbonate and with ethyl orthoformate.

The aim of the present investigation was to study the interaction of ethynylvinyl alkyl ethers with trialkylchlorosilanes. Synthesis of the trialkylsilylethynylvinyl alkyl ethers was accomplished through the organomagnesium derivatives, which were prepared in ether rather than in the tetrahydrofuran solution of Dornow and Ische:

$$C_2H_5MgBr + HC \equiv C - CH = CHOR \rightarrow BrMgC \equiv C - CH = CHOR; \quad (2)$$

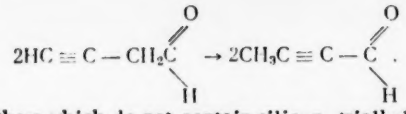
$$BrMgC \equiv C - CH = CHOR + R_3SiCl \rightarrow R_3SiC \equiv C - CH = CHOR + MgClBr. \quad (3)$$

Reactions (2) and (3) take place under very mild conditions.

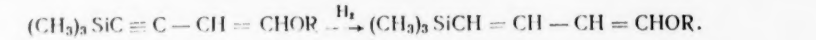
The trialkylsilylethynylvinyl butyl ethers obtained in this manner are reminiscent, with respect to chemical properties, of ethynylvinyl alkyl ethers which do not contain silicon (they too are easily hydrolyzed by 2% H_2SO_4), but they do have their own peculiarities. When the trialkylsilylethynylvinyl alkyl ethers were hydrolyzed for the purpose of proving their structure, it was found that cleavage occurred at an Si–C bond:

$$2(CH_3)_3SiC \equiv C - CH = CHOR \xrightarrow[H_2O]{H^+} (CH_3)_3SiOSi(CH_3)_3 + 2CH \equiv C - CH_2C\begin{matrix}O\\ \\H\end{matrix}.$$

The resulting 1-butyn-4-al isomerizes to tetrolaldehyde:

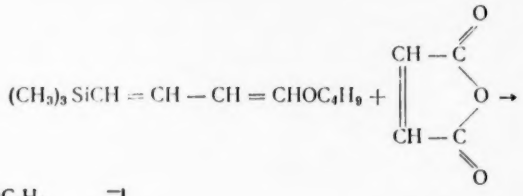


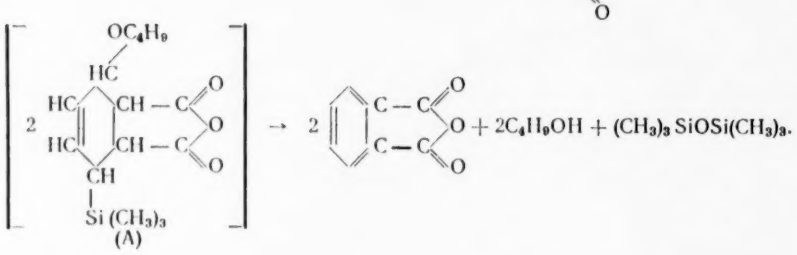
In contrast to ethynylvinyl alkyl ethers which do not contain silicon, trialkylsilylethynylvinyl alkyl ethers are not hydrogenated over $PtO_2 \cdot H_2O$ or Pd deposited on calcium sulfate [15], and are hydrogenated over a mixture of 2% Pd/$CaCO_3$ and 5% Pt/C. Stepwise hydrogenation gave trimethylsilyl-4-butoxy-1,3-butadiene:



Condensation of the latter with maleic anhydride gave adduct (A), and subsequent cleavage [16] led to the formation of butyl alcohol and trimethylsilanol, which under the conditions employed, gave hexamethyldisiloxane.

It was established that the final addition product was phthalic anhydride.





(A)

The silicon-containing ethynylvinyl butyl ether did not form trimethylsilyl-1-butyn-4-al when heated with butanol, either in the absence of a catalyst or in the presence of 1-2% of a basic or acid catalyst.

TABLE 1

Name of ether	B. p., °C/mm	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Found, % C	Found, % H	Found, % Si	Calculated, % C	Calculated, % H	Calculated, % Si
Ethynylvinyl butyl ether*	61,5°/12	1,4712	0,8664	40,04	38,16	77,1	9,70	—	77,36	9,85	—
Trimethylsilylethynylvinyl butyl ether	110—112°/15	1,4695	0,8589	63,73	63,68	67,05	10,23	14,12	67,28	10,27	14,30
Triethylsilylethynylvinyl butyl ether	105—106°/7	1,4895	0,8886	77,10	77,57	70,40	10,90	11,82	70,52	11,01	11,78

*The acetal was isolated in addition to the ether.

EXPERIMENTAL

Synthesis of ethynylvinyl butyl ether. A 2% alcoholic solution of KOH was placed in a round bottom flask fitted with a stirrer and a reflux condenser. The system was purged with dry nitrogen, the reaction mixture was heated to 70-75°, and diacetylene, carried in a stream of dry nitrogen, was then passed into the reaction

mixture. Upon completion of the reaction, the mixture was washed three or four times with water, dried with calcined potassium carbonate, and distilled under vacuum. The characteristics of the ethynylvinyl and trialkylsilylethynylvinyl butyl ethers prepared are shown in Table 1.

Synthesis of trimethylsilylethynylvinyl butyl ether. $(CH_3)_3SiC{\equiv}C-CH = CHOC_4H_9$. Ethylmagnesium bromide was prepared from 2.9 g of magnesium and 13.1 g of C_2H_5Br in a three-neck flask fitted with a stirrer, a reflex condenser, a dropping funnel, and a thermometer. To the ethylmagnesium bromide, cooled to −10°, was added dropwise and with stirring 14.5 g of ethynylvinyl butyl ether, which was at room temperature. The mixture was stirred at 20° for 4-5 hours, and 13 g of trimethylchlorosilane was then added dropwise. Stirring was continued for an hour, and the mixture was then allowed to stand overnight. On the following day, the reaction mixture was stirred for another 3 hours, the precipitate was filtered, and the filtrate was distilled in a stream of nitrogen. The following fractions were collected during the distillation: I) 24-38°/14 mm; II) 110-112°/15 mm.

Fraction I was unreacted trimethylchlorosilane, slightly contaminated with trimethylsilylethynylvinyl butyl ether.

Fraction II, 13.6 g (50.7% yield), was trimethylsilylethynylvinyl butyl ether, b. p. 110-112°/15 mm, n_D^{20} 1.4695; d_4^{20} 0.8589. MR_D found 67.73; calculated,* 63.68.

Found %: C 67.05; H 10.23; Si 14.12. Calculated % for $C_{11}H_{20}OSi$: C 67.28; H 10.27; Si 14.30.

Triethylsilylethynylvinyl butyl ether was synthesized under analogous conditions with a yield of 52.3%; b. p., 105-106°/7 mm; n_D^{20} 1.4895; d_4^{20} 0.8886; MR_D found 77.16, calculated, 77.57.

Found %: C 70.40; H 10.90; Si 11.82. Calculated % for $C_{14}H_{26}OSi$: C 70.52; H 11.01; Si 11.78.

Hydrolysis of trimethylsilylethynylvinyl butyl ether. a) A thin-walled ampoule containing 0.1-0.2 g of the ether was placed in a 200-ml flask containing 25 ml of 2% H_2SO_4 and 15 ml of $NaHSO_3$. The flask was sealed, the ampoule containing the ether was broken by vigorous stirring, and the reaction mixture was allowed to stand for 30 minutes. The $NaHSO_3$ which had not reacted with aldehyde was titrated with 0.1 N iodine solution. Hydrolysis amounted to 74%. Under these conditions, 79.5% of the triethylsilylethynylvinyl butyl ether was hydrolyzed.

b) A mixture of 3 g of trimethylsilylethynylvinyl butyl ether and 10 ml of 2% H_2SO_4 was heated, with stirring, at 50° for 1 hour in a flask fitted with a reflux condenser, a stirrer, and a thermometer. The reaction mixture was dissolved in ethanol, and a freshly prepared solution of 2,4-dinitrophenylhydrazine was added. The mixture was allowed to stand overnight. The resulting 2,4-dinitrophenylhydrazone was filtered and recrystallized from ethanol. This procedure gave the 2,4-dinitrophenylhydrazone of tetrolaldehyde with an m. p. of 135°. The literature [17] gives a value of 136° for the m. p. of tetrolaldehyde 2,4-dinitrophenylhydrazone. The sample did not depress the melting point of a known sample.

Analytical data for the hydrazone:

Found %: C 48.25, 48.17; H 3.32, 3.25; N 22.36, 22.62. Calculated % for $C_{10}H_8N_4O_4$: C 48.39; H 3.24; N 22.57.

Stepwise hydrogenation of trimethylsilylethynylvinyl butyl ether. A mixture consisting of 2% $Pd/CaCO_3$ and 5% Pt/C catalysts and 4 g of the ether was placed in a hydrogenation bomb. The air was purged from the bomb with hydrogen, and the hydrogenation was begun. The hydrogenation was interrupted with 540 ml of hydrogen (22°, 743 mm) had been absorbed. The theoretical consumption of hydrogen under these conditions is 510 ml of hydrogen. The catalyst was removed by filtration, the methanol was distilled, and the resulting product was distilled in a stream of nitrogen. The resulting product boiled at 88-89°/7 mm; n_D^{20} 1.4580; d_4^{20} 0.8532. MR_D found 63.45, calculated 63.52. The yield was 57% of theoretical (2.28 g).

Condensation of $(CH_3)_3SiCH = CH - CH = CHOC_4H_9$ with maleic anhydride. To a flask fitted with a reflux condenser and a thermometer was charged 1.5 g of 1-trimethylsilyl-4-butoxy-1,3-butadiene (b. p. 88-89°/7 mm; n_D^{20} 1.4580), and a solution of 2 g of maleic anhydride in 50 ml of benzene was added. No heat of

*The molar refraction was calculated using a value of 3.8 for the group contribution of $-C{\equiv}C-C{=}C$.

reaction was observed. The mixture was heated on a water bath for 1 hour, the benzene was then distilled off, and the residue was distilled. The following fractions were collected: I) 96-99°/25 mm; II) 156-162°/25 mm.

Fraction I was unreacted maleic anhydride. Fraction II was recrystallized from petroleum ether, and 0.27 g of adduct (25.7% yield) with an m.p., of 130° was obtained. A mixture of the adduct with a known sample of phthalic anhydride showed no depression of the melting point.

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THE FORM OF THE EQUILIBRIUM DIAGRAMS OF Ni–NiAl–Mo ALLOYS

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Nickel-based alloys are of great significance as regards alloys operating at high temperatures and loads [1, 2]. Alloys having high-temperature strength may be sought for in the system Ni–Al–Mo particularly [3]; more complex high temperature alloys based on the nickel–chromium system with the addition of Al, Ti, Mo, and Co ("nimonik-100," "yudimet-500," and others [2]) have been successfully used. Nevertheless, up to the present not even the ternary equilibrium diagram for Ni–Al–Mo alloys has been constructed, not to mention diagrams for more complex polycomponent nickel alloys containing Al and Mo. In the bibliographic publication on alloys [4], as well as in the more recent work [14], there is reference to only a single work in which the Ni–Al–Mo equilibrium diagram was studied. However, the schematic distribution of phase fields in the nickel corner of the diagram presented in this single work [5] was determined only on the basis of a study of the microstructure of the alloys (without phase identification), and the alloys were known not to have reached the equilibrium state (the samples were subjected to annealing for 3-10 hours at 700°). Moreover, the equilibrium diagrams of the binary systems Ni–Al and Ni–Mo were not accurately known at that time (1925). Therefore, it is natural that the distribution of phase fields presented in reference [5] is not the actual distribution, as the data which we have obtained show. In the paper mentioned above [3], only the high-temperature properties of Ni–Al–Mo alloys were studied, and no attempt was made to construct the equilibrium diagram; however, it followed from this work that the singular system Ni–Al–NiMo can be isolated from the complete Ni–Al–Mo system. As will be seen below, this supposition is incorrect, and in actuality the singular system is the system Ni–NiAl–Mo, similarly to the case in the equilibrium diagrams of the systems Ni–Al–Cr [6-8] and Ni–Al–W [9].

The alloys used in our work were fused from pure materials in a high-frequency furnace; alloys with a Mo content of more than 50 atom % could not be prepared owing to their high melting points. The fusions were carried out in an atmosphere of argon in corundum crucibles without tapping. In order to avoid liquation of compositions, the fused ingots were again remelted, but in the reverse position. Seven alloys of the binary Ni–Mo system (denoted by the letters a to g in Table 1) and 30 alloys of the ternary system (denoted by numerals) were fused. The compositions (in atom %) of the alloys are given as determined by the compositions of the charges, since chemical analysis showed that deviations in the content of each element from those given did not exceed 1 atom % in the majority of cases.

The alloys were homogenized at 1200° in a vacuum furnace for 100 hours; the alloys richest in Al (which contained the greatest amounts of NiAl) were homogenized once more at 1500° (2 hours), since after the first homogenization, a dendritic structure was still clearly visible in the sections.

It was proposed to study the alloys along three isothermal sections: those at 1200, 1000, and 800°; in accordance with this proposal, three groups of samples were given the following heat treatments:

1) 1200° – 100 hours → quenching;

2) 1200° – 100 hours + 1000° – 100 hours → quenching;

3) 1200° – 100 hours + 1000° – 100 hours + 800° – 100 hours → quenching.

The investigation of these alloys was carried out by parallel microstructural and x-ray methods, since each of these methods individually either does not provide reliable identification of the phases (the microstructural method*), or does not make apparent small amounts of the second and third phases (the x-ray method**). The

TABLE 1

Number of Phases According to Microstructural Analysis and Phase Identification (by Means of X-ray Data) in the Alloys Investigated after Quenching from 1200°

Alloy	Content, in atom.%		No. of phases	Phases	Alloy	Content, in atom.%		No. of phases	Phases
	Mo	Al				Mo	Al		
a	7	—	1	γ	12	18	2½	1	γ
b	16	—	1	γ	13	21	2½	1	γ
c	20	—	1	γ	14	20	5	1	γ
d	25	—	1	γ	15	17½	10	2	α + γ
e	28	—	2	γ + (δ)	16	15	20	2	α + γ′
f	38	—	2	γ + δ	17	5	47½	2	α + β
g	48	—	2	(γ) + δ	18	10	45	2	α + β
1	10	20	2	α + γ′	19	20	40	2	α + β
2	10	15	3	(α)+γ+γ′	20	30	35	2	α + β
3	10	5	1	γ	21	25	30	2	α + β
4	5	25	3	(α)+β+γ′	22	20	25	3	α + (β) + γ′
5	5	10	1	γ	23	40	20	?	α + γ′
6	2½	10	1	γ	24	45	10	?	α + γ(γ′)
7	2½	22½	2	γ + γ′	25	30	5	2	α + γ
8	2½	25	1	γ′	26	5	2½	2	α + γ′
9	7½	10	1	γ	27	2½	40	2	(α) + β
10	12½	5	1	γ	28	2½	48	2	α + β
11	15	5	1	γ	29	50	2½	2	α + γ
					30	10	12½	1	γ

Note: The parentheses indicate that lines for the enclosed phases were not observed on the x-ray patterns.

results obtained for quenching temperatures of 1000 and 800° were not sufficiently reliable (except for the γ-region), apparently as a consequence of the insufficiency of the 100-hour annealing time at these temperatures; the results obtained for a quenching temperature of 1200° are presented in Table 1. The isothermal sections corresponding to these data are shown in Fig. 1; the figure also shows the boundaries of the γ-regions at 800 and 1000°. Data on the binary systems Ni–Al [7, 10] and Ni–Mo [11] were used in the construction of the diagram. (The data on these binary systems are in good agreement with our results on the binary alloys a to g at 1200°). It was not possible to detect the compounds Ni_4Mo (β_1-phase) and Ni_3Mo (γ_1-phase) in the binary system, although they should have been formed at 800° in the alloys containing 20 and 25 atom.% Mo, respectively [11]. The δ-phase (NiMo) was the predominant phase in alloy g at all three temperatures; this shows up well on the x-ray patterns (Fig. 2a). Judging from the data in Pearson's handbook [12], the compound Ni Mo has a complex tetragonal structure (a = 9.108, c = 8.852 Å) with 56 atoms in the unit cell. In view of the fact that detailed data on this structure were presented by other authors (Shoemaker, Brink, and Fox) only in the report in reference [13] and in the discourse in reference [12] and still have not been published in a journal, we present in Table 2 the reflection angles found by us for the δ-phase (using K_α Cu-radiation) and the individual line intensities are also shown.*** These data should be useful for identification of the δ-phase in other alloys.

*For example, the α-phase based on Mo was apparently taken as the compound NiMo on the photomicrographs in reference [3].

**Moreover, in a given case the x-ray method does not always differentiate the γ-phase (solid solution based on Ni) and the γ′-phase (solid solution based on the compound Ni_3Al).

***The lines could not be reliably indexed with the structure assumed for the α-phase, since the theoretical x-ray pattern constructed with only a knowledge of the dimensions of the unit cell contains a colossal number of lines, the ratios of the intensities of which are not known.

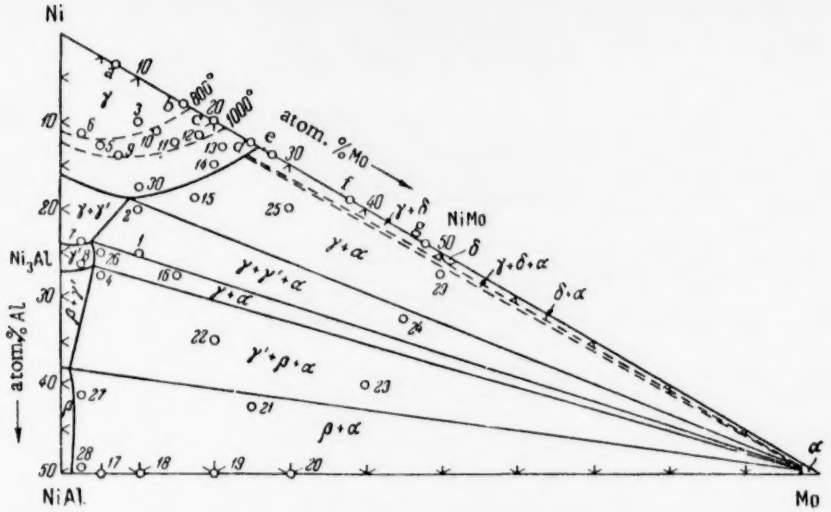

Fig. 1. Isothermal section of part of the equilibrium diagram of Ni–Al–Mo alloys at 1200°; the section was constructed from the experimental data. The numerals next to the circles indicate the number of the alloy.

TABLE 2

Reflection Angles and Line Intensities of the δ-Phase on X-Ray Patterns Obtained with K_α Cu Radiation

ϑ^0	Intensity	ϑ^0	Intensity	ϑ^0	Intensity	ϑ^0	Intensity
27.2	w.	38.7	av.	52.8	w.	66.1	w.
28.6	av.	39.6	w.	55.4	v. w.	68.0	w.
30.6	s.	40.6	w.	57.2	v. w.	69.0	w.
31.2	v. w.	41.3	w.	57.6	v. w.	69.8	w.
21.8	v. w.	43.6	v. w.	58.8	w.	70.4	w.
32.1	s.	45.0	av.	59.8	v. w.	71.6	w.
3.0	av.	46.1	av.	60.8	v. w.	72.8	w.
3.7	av.	47.1	av.	61.8	v. w.	75.6	v. w.
34.7	w.	48.8	w.	62.6	v. w.	76.8	v. w.
23.9	av.	49.8	v. w.	63.4	v. w.	78.0	v. w.
5.3	av.	50.8	v. w.	64.2	v. w.	80.4	v. w
7.4	av.	51.6	v. w.	65.3	av.	81.6	w.
8.2	av.						

It is interesting that the δ-phase dissolves almost no Al; indeed, alloy 29, which contained a total of only $2\frac{1}{2}$ atom.% Al, consisted of γ- and α-phases (the latter being a solid solution based on Mo) (Fig. 2, b). These two systems of lines are visible on the x-ray pattern of alloy 15. Hence, it follows directly that the existence of both a two-phase region Ni_3Al + NiMo (γ' + δ), and a three phase region of the solid solution Ni + Ni_3Al + NiMo (γ + γ' + δ), which was proposed in reference [3], is impossible. The data presented in this reference for the two alloys 16 atom % Mo and 18 atom % Al (heat treatment at 1150°) and 9 atom % Mo and 25 atom % Al (heat treatment at 1250°) are in good agreement with our data for 1200° (Fig. 1), if it is assumed that in reference [3] indications in the microsections were erroneously assumed to belong to the α-phase rather than the δ-phase (NiMo). The position of the three-phase region γ + δ + α is indicated in Fig. 1 by a broken line owing to insufficient experimental data.

As may be seen from the data of Table 1, the results of the x-ray investigation and the microstructural investigation are basically in agreement provided the amount of the phase is not too small to be detected by the

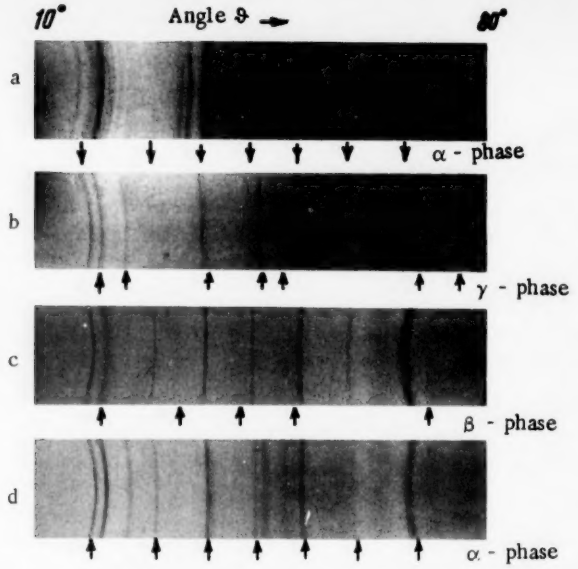

Fig. 2. X-ray patterns of Ni–Al–Mo alloys quenched at 1200°. a) Binary alloy g: Ni + 48 atom.% Mo (δ-phase); b) alloy 29: Ni + 50 atom.% Mo + 2.5 atom.% Al (α + γ); c) alloy 21: Ni + 25 atom.% Mo + 30 atom.% Al (α + β); d) alloy 16: Ni + 15 atom.% Mo + 20 atom.% Al (α + γ'). Filtered K_α Cu radiation.

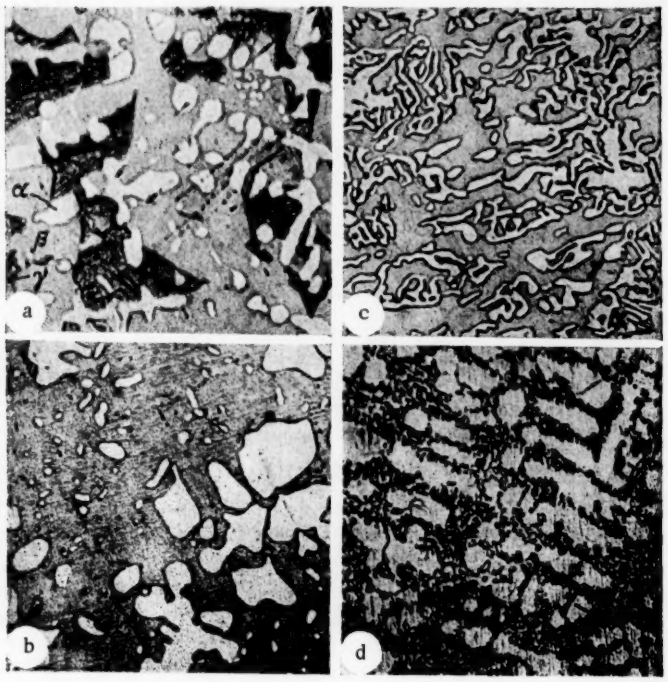

Fig. 3. Microstructure of Ni–Al–Mo alloys quenched at 1200°. a) Alloy 22: Ni + 20 atom.% Mo + 25 atom.% Al (α + β + γ'); b) alloy 29: Ni + 50 atom.% Mo + 2.5 atom.% Al (α + γ); c) alloy 21: Ni + 25 atom.% Mo + 30 atom.% Al (α + β); d) alloy 16: Ni + 15 atom.% Mo + 20 atom.% Al (α + γ'). Marble's etchant, 300 X.

x-ray method. The only exceptions are alloys 22 and 23, in which the β-phase (based on the compound NiAl) was not detected by the x-ray method although alloy 22, for example, was clearly three-phase (Fig. 3,a): α + β + γ'; however, for alloys 17 and 18, in which this phase was present in significantly larger amounts as a mixture with the α-phase, and for alloys 19-21 the lines of the β-phase were not readily visible on the x-ray patterns (they were very diffuse as compared to the lines of the isomorphic α-phase, Fig. 2, b) in spite of the fact that the β-phase was quite apparent on the photomicrographs (Fig. 3 a and b). For some unknown reason, it was not possible to develop the microstructure of alloys 23 and 24. The γ and γ' phases, on the contrary, could be discerned only on the photomicrographs (Fig. 3, b and d), while they give identical patterns on the x-ray pictures (Fig. 2, b and d). It should be noted that Mo was appreciably soluble in the γ'-phase – not less than 2½ to 3 atom.% – since alloy 8 was single-phase (γ'). It was assumed in reference [14] that the solubility of Mo in the γ'-phase is much less (<1 atom. %).

In conclusion, we point out that the isothermal section of the Ni–NiAl–Mo system at 1200° is analogous to the isothermal section of the Ni–NiAl–Cr system at temperatures below 1000°; according to the data of reference [6], an equilibrium of the γ'- and α-phases exists below this temperature in the Ni–NiAl–Cr system as in the system studied in the present work. Above this temperature, the γ- and β-phases coexist in the Ni–NiAl–Cr system, which is similar to the situation in the related Ni–NiAl–W system [9].

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CATALYTIC DEHYDROGENATION OF ISOPROPYLBENZENE

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Derivatives of aromatic hydrocarbons in which there is an unsaturated side chain have found widespread application in the synthetic rubber and plastics industries and in other fields of the national economy. The cheapest and most convenient method of obtaining these monomers is by catalytic dehydrogenation of alkylbenzenes, and this method has acquired considerable practical importance. A. A. Balandin and G. M. Marukyan [1] investigated the dehydrogenation of isopropylbenzene over copper–chromium catalyst with carbon dioxide dilution. The yield of α-methylstyrene at 625° was 50% based on the isopropylbenzene fed. An α-methylstyrene yield of about 71% at a total conversion of 44% has been obtained by dehydrogenation of isopropylbenzene over chromia-alumina and iron-magnesia catalysts at 625° in the presence of steam diluent [2].

The aim of the present work was to study the reaction kinetics and the effect of the structure of the hydrocarbon molecule on the reaction rate. The experiments were carried out in a flow system with a mixed oxide catalyst [3] in the presence of steam diluent. The quartz reaction tube contained 10 ml of catalyst. The hydrocarbon and water were fed by means of an automatically controlled injector. The steam was preheated to 300°

TABLE 1

Dehydrogenation of Isopropylbenzene; Feed Rate 0.42 ml in Three Minutes (800 ml/liter/hour). Steam Dilution 1 : 2 (weight)

Catalyst particle size, mm	Temp., °C	n_D^{20} of catalyzate	α-Methylstyrene in catalyzate	H_2 (S. T. P.) in 3 min	Degree of dehydrog. from H_2 prod., %	Gas analysis, vol., %		
						CO_2	C_nH_{2n}	H_2
1,5	516	1,4963	12,0	7,7	11,4	0,4	None	99,6
	520	1,4981	15,5	9,8	15,1	2,0	»	98,0
	544	1,5051	30,0	20,6	30,1	4,4	»	95,2
	550	1,5096	39,5					
	568	1,5196	59,0	42,9	67,5	4,2	0,6	95,0
	582	1,5250	70,5	54,7	81,0	5,8	0,6	95,0
3,0	516	1,4958	13,0	6,5	10,1			
	528	1,5000	19,5	12,0	18,2	1,6	None	98,0
	544	1,5051	30,0	20,5	31,8	2,6	0,4	96,5
	550	1,5069	34,0	20,8	31,6	2,4	0,4	97,0
	562	1,5143	49,0	33,6	50,9	4,2	0,8	
	607	1,5310	83,0	72,1		9,0	2,0	88,5
5,0	524	1,4991	17,5	11,8	17,2	0,8	—	99,0
	538	1,5033	27,5	18,0	27,3	1,8	—	98,2
	546	1,5061	32,0	23,4	34,7	5,6	0,2	94,0
	554	1,5110	42,5	27,1	41,1	2,2	0,2	96,6
	566	1,5157	52,0	38,8	57,4	5,2	—	94,8

before entering the reaction tube. The extent of steam dilution was maintained constant in all experiments and amounted to 1 : 2 (weight). The liquid products were condensed in a receiver, and the gas was collected in a graduated cylinder. The volume of gas was measured over a three-minute interval with an accuracy of 2 ml, and the volumes were converted to standard conditions (S. T. P.). The CO_2 content of the gas was determined by absorption in KOH solution; the unsaturates were determined with a solution of mercuric sulfate in sulfuric acid; and the hydrogen and saturated hydrocarbons were determined by combustion over cupric oxide. The catalyzate was colorless. The α-methylstyrene content of the catalyzate was determined by index of refraction, and the results were checked by the bromine number method of Rosenmund [4]. There was close correspondence between the amount of hydrogen produced and the amount of α-methylstyrene formed (Table 1). The catalyst was purged with steam-air mixture and with air for 30 minutes after each experiment. Catalyst activity was checked after each series of experiments by dehydrogenation of isopropylbenzene under standard conditions, and the activity was found to remain constant over the duration of the experiments. The original isopropylbenzene boiled at 152.5-153°, d_4^{20} 0.8620, n_D^{20} 1.4947; literature values: b. p. 152.5°, d_4^{20} 0.8620, n_D^{20} 1.4947 [5, 6].

The dehydrogenation kinetics of isopropylbenzene were investigated at temperatures of 500-550° and a feed rate of 0.42 ml in 3 minutes, which corresponds to a space rate of 800 ml/liter of catalyst/hour. The reaction rate was determined from the amount of hydrogen produced. The effluent gas consisted mainly of hydrogen with small amounts of CO_2 (from 0.5 to 2.0%) and unsaturated hydrocarbons (up to 0.4%). Saturated hydrocarbons were not found in the gas (Table 1). As in the work reported in reference [7], the reaction rate constants were calculated from the experimental data by means of the formula

$$\frac{dx}{dt} = k\frac{[A_1]}{[A_1] + z_2[A_2] + z_3[A_3]} \qquad (1)$$

in a form suitable for use with data obtained in a flow system [7], where z_2 and z_3 are the relative adsorption coefficients of the reaction products. In order to determine the relative adsorption coefficients, experiments on the rate of dehydrogenation of binary mixtures of isopropylbenzene and α-methylstyrene and of isopropylbenzene and hydrogen were carried out under analogous conditions. Calculation of the relative adsorption coefficients was carried out by the formula given in reference [8]. The relative adsorption coefficient values thus obtained are shown in Table 2, from which it can be seen that the value of z_2 for α-methylstyrene changes from 3.8 at 520° to 0.95 at 550°. The value of z_3 for hydrogen, 0.7, does not change with temperature. Figure 1, which was plotted from the data of Table 1,

TABLE 2

Rate of Constants for the Dehydrogenation of Isopropylbenzene, k_C and Thermodynamic Functions for the Adsorptive Displacement of Isopropylbenzene by α-Methylstyrene

Temp °C	z_2	k_c, ml/min.	−ΔF, cal/mole	ΔH, cal/mole	ΔS, cal/°C/mole
520	3,8	0,7759	2092	60,0	77,
530	2,4	0,9790	1395		74,6
540	1,5	1,227	654		72,8
550	0,95	1,570	−83		71,0

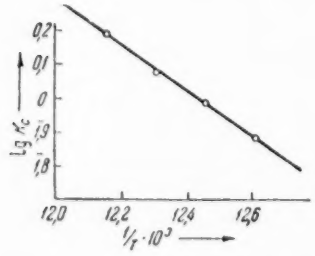

Fig. 1. Logarithm of the reaction rate constant as a function of 1/T.

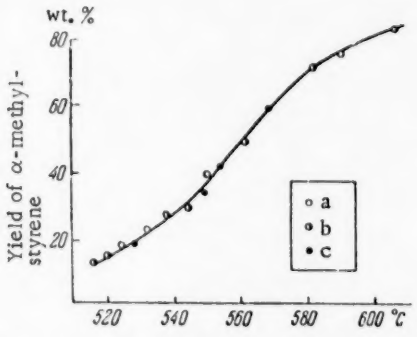

Fig. 2. Effect of catalyst particle size on the yield of α-methylstyrene at different temperatures. a) 1.5 mm; b) 3.9 mm; c) 5.0 mm.

shows the relationship between the logarithm of the reaction rate constant and the reciprocal of the absolute temperature. The points fall on a straight line – the Arrhenius law is obeyed. The activation energy calculated from the reaction rate constants is 30.3 kcal/mole, and the preexponential constant is log k_0 = 6.25.

With the aim of determining the region – kinetic or diffusion – in which the catalyst functions, experiments were carried out with catalysts of different particle sizes. The grain diameters were 1.5, 3, and 5 mm (Table 1). The experiments showed that the particle size of the catalyst had no effect on the process. Figure 2 shows the dependence of α-methylstyrene yield on temperature for various samples of catalyst. All of the points lie on the same curve. Hence, it may be concluded that the experiments were carried out in the kinetic region. The changes in free energy, ΔF, heat content, ΔH, and entropy, ΔS, during adsorptive displacement from the active dehydrogenation centers were calculated from the values of the relative adsorption coefficients.

In addition to the investigation of the dehydrogenation reaction kinetics, experiments were carried out with isopropylbenzene at higher temperatures. It was found that the degree of dehydrogenation of isopropylbenzene increased with an increase in temperature. At temperatures of 580 and 607° and a feed rate of 800 ml/liter/hour, the yield of α-methylstyrene was, respectively, 70.5 and 83% based on the hydrocarbon fed (Table 1). The results obtained in the present work are of definite practical interest.

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ESTERS OF THIOSULFONIC ACIDS – NEW FUNGICIDAL AGENTS

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The antimicrobial activity of esters of thiosulfonic acids (I), which have been known since the second half of the last century, has only recently been studied [1], although these compounds are structurally related to esters of thiosulfinic acids (II), which include the natural antibiotic allicin.

$$\underset{\text{(I)}}{R{-}SO_2{-}S{-}R'} \qquad \underset{\text{(II)}}{R{-}SO{-}S{-}R'}$$

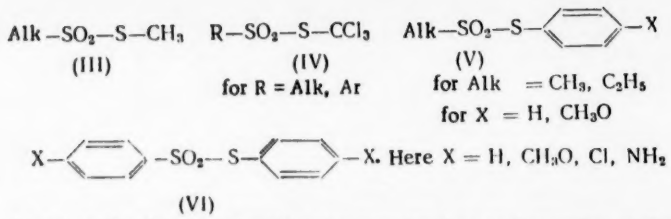
Like the compounds (II), the esters of thiosulfonic acids possess a broad spectrum of antimicrobial action, and in experiments in vitro they have shown bacteriostatic and bacteriocidal action on gram-positive, gram-negative, and acid-resistant bacteria, various fungi, protozoa, etc.; an investigation carried out at the Institute of Microbiology, Academy of Sciences USSR, with 35 species of microorganisms gave positive results in all cases [1].

Esters of thiosulfonic acids exhibited even higher activity during a study of their action on 40 different strains of 22 species of phytopathogenic bacteria [2]; at the same time, they have also displayed properties of plant growth stimulators, on the strength of which, the use of these esters (I) as agents for the treatment, prior to sowing, of seeds of grains, truck garden crops, and industrial corps produces a sharp decrease in the susceptibility of the plants to bacteriosis, shifts the phase of their development toward earlier ripening, and, on the whole, increases the yield.

A fungicidal effect of these same compounds – a decrease in diseases of the heads of barley, corn, etc. – has been observed during field experiments.

For this reason, we considered that a study of the fungicidal properties of esters of thiosulfonic acids would have widespread interest, and so we undertook the present investigation. As subjects for investigation we first selected alkyl esters of alkanethiosulfonic acids, particularly the methyl ester (III), which possess the highest antimicrobial activity.

It also appeared to be of interest to study the fungicidal properties of the trichloromethyl esters (IV), which, according to the data of American investigators [3], have high fungicidal activity. The latter seemed to us even more deserving of attention, since we did not consider it possible to agree with the opinion of these authors regarding the equivalence of the fungicidal properties of trichloromethyl esters of different thiosulfonic acids regardless of the nature of the radical R (Formula IV). According to the results of our earlier investigation [1], it would be expected that trichloromethyl esters of alkanethiosulfonic acids would have a higher activity than the analogous esters of arenethiosulfonic acids.



(III) (IV) for R = Alk, Ar (V) for Alk = CH_3, C_2H_5 for X = H, CH_3O

(VI) Here X = H, CH_3O, Cl, NH_2

This selection of subjects for the investigation also permitted us to determine at the same time the effect of the trichloromethyl group itself (by replacement of the hydrogens of the methyl group by chlorine atoms) on the fungicidal properties of esters of thiosulfonic acids.

TABLE 1

Fungicidal Activity of Esters of Thiosulfonic Acids, $R-SO_2-S-R'$

Expt. No.	R	R'	Conc. of active principle in prepn., %	Suppression of growth of fungi as compared to control, %				
				Diplodia zeae	Alternaria tenuis	Verticillium dahliae	Fusarium sclerotium	Fusarium oxysporum
1	iso-C_3H_7	CH_3	0,02	100	79	100	100	82
			0,01	100	70	100	48	53
2	C_4H_9	CH_3	0,02	100	90	100	100	100
			0,01	100	80	100	100	100
3	iso-C_4H_9	CH_3	0,02	100	90	100	100	100
			0,01	100	60	100	100	100
4	iso-C_3H_7	CCl_3	0,02	100	100	100	100	100
			0,01	100	92	100	100	100
5	C_4H_9	CCl_3	0,02	100	100	100	100	100
			0,01	100	92	100	100	100
6	iso-C_4H_9	CCl_3	0,02	100	100	100	100	100
			0,01	100	79	100	100	100
7	p-ClC_6H_4	CCl_3	0,05	53,8	100	100	61,6	100
			0,01	0,0	74,4	72,0	48,1	22,8
8	p-$CH_3CONHC_6H_4$	CCl_3	0,05	18,8	71,8	100	100	35,9
			0,01	16,3	64,2	16,0	77,0	5,7
9	p-$NO_2C_6H_4$	CCl_3	0,025	0,0	68,6	60,0	32,7	23,3
			0,01	0,0	51,5	26,7	9,7	7,2
10	CH_3	C_6H_5	0,04	100	100	100	100	84
			0,02	90,3	80,0	76,2	60,0	56,7
11	CH_3	p-$CH_3OC_6H_4$	0,04	94,0	80,0	100	85,0	26,7
			0,02	70,0	74,3	67,0	60,0	55,0
12	C_2H_5	C_6H_5	0,04	100	98	100	97	84
			0,02	92,7	80,0	76,2	71,0	54,0
13	The same	p-$CH_3OC_6H_4$	0,04	96,6	82,0	100	100	79,0
			0,02	92,0	76,0	57,0	80,0	63,0
14	C_6H_5	C_6H_5	0,05	95,0	61,6	100	55,0	60,0
			0,01	40,0	56,5	72,0	32,7	49,1
15	p-ClC_6H_4	p-ClC_6H_4	0,025	47,3	74,4	33,4	42,4	43,0
			0,01	43,7	68,6	33,4	34,7	32,2
16	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4$	0,04	87,4	67,0	63,0	60,0	52,0
			0,02	82,8	64,0	44,0	52,1	43,0
17	p-$NH_2C_6H_4$	p-$NH_2C_6H_4$	0,025	93,1	85,8	73,4	71,2	64,3
			0,01	90,3	74,4	60,0	42,4	43,0
18	Phygon (standard)		0,025	93,6	97,2	100	100	50,0
			0,01	88,1	85,8	100	92,4	39,3
19	Captan (standard)		0,03	85,1	76,0	77,0	79,4	79,4
			0,02	83,6	72,0	65,0	65,6	53,5
20	Tsineb (standard)		0,04	73,2	68,0	100	22,5	22,5
			0,02	15,0	24,0	15,0	5,2	6,9

Certain aryl esters (V) and (VI) of alkane- and arenethiosulfonic acids were also included among the subjects for investigation, which permitted a more complete determination of the connection between the structure and the fungicidal activity of this class of compounds.

The study of the fungicidal activity of these esters of thiosulfonic acids was carried out in the toxicological laboratory of the Ya. V. Samoilov Scientific Institute of Fertilizer and Insectofungicides. Five species of fungi were used – Diplodia zeae, Alterneria radicina, Verticillium dahliae, Fusarium vasinfectum, and Fusarium oxysporum. The laboratory experiments were carried out by introducing the preparations in the form of acetone solutions of definite concentrations into the nutrient agar medium on which the fungi were then sown; the results of the effect of the esters were determined after five days of growth of the fungi. For comparison, analogous experiments were carried out with Phygon, Captan, and Tsineb at the same concentration of active principle.

The results of the investigation, which are presented in Table 1, completely confirm our supposition. They show that trichloromethyl esters of alkanethiosulfonic acids are the most active fungicides of all of the compounds (I) studied in the present work; their effect on fungi in the in vitro experiments was considerably greater than that of the analogous esters of arenethiosulfonic acids.

However, the trichloromethyl group was not responsible for the fungicidal activity of these compounds. Replacement of the chlorine atoms by hydrogen atoms and the resulting conversion to methyl esters of alkanethiosulfonic acids had little effect on the activity of these compounds; like the trichloromethyl esters of alkanethiosulfonic acids, the methyl esters exhibited a considerably greater effect on the fungi than did the trichloromethyl esters of arenethiosulfonic acids.

The particular effect of the nature of the radical R also appeared during further conversion to aryl esters of thiosulfonic acids (V) and (VI). While, as indicated previously, the aryl esters of methane- and ethanethiosulfonic acids (Nos. 10-13, Table 1) displayed high fungicidal activity and even exceed in activity the trichloromethyl esters of arenethiosulfonic acids (Nos. 7-9, Table 1), the aryl esters (VI) had appreciably lower activity than the remaining esters (I). However, even in this case certain of them (No. 17, Table 1) were not inferior in their action to such an active fungicide as Captan at the same concentration of active principle.

The results obtained in the present work permit us tp assert that esters of thiosulfonic acids, particularly esters of alkanethiosulfonic acids, are highly active fungicides and deserve a more detailed investigation.

Future field experiments should develop the possibilities and prospects for their use in agriculture.

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PREPARATION OF VINYLPHENOLS BY CATALYTIC CRACKING OF CERTAIN DIHYDROXYDIARYLALKANES

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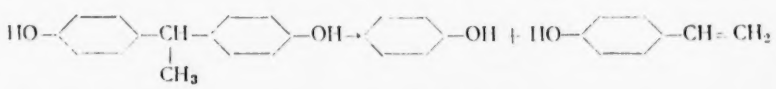
In connection with the development of the chemistry of high polymers, investigations relating to the synthesis of new, highly reactive monomers have acquired great significance. Vinylphenols constitute a group of such monomers, but the synthesis of many of these have either not been accomplished up to the present time or have received very little study. The scientific literature contains the most contradictory information relative to the possibility of synthesizing and the effectiveness of syntheses of these compounds. Thus, in 1955, Bader [1], studying a previously proposed method for the preparation of o-vinylphenol by condensation of phenol with ethylene oxide or ethylene chlorohydrin [2], reported that o-vinylphenol cannot be prepared by this method. The conclusion of Bader was subsequently confirmed [3]. Another vinylphenol isomer, p-vinylphenol, was isolated from natural materials and first characterized in work reported in reference [5]; however, attempts to synthesize this compound have been unsuccessful until recently. It was not until 1958 that p-vinylphenol was prepared synthetically (from phenol through p-acetoxyacetophenone [5]), but the method is very complex, consisting of five stages, and is significant only in a preparative sense. The synthesis of other vinylphenols has been studied to an even lesser extent.

We now propose a new method for the preparation of vinylphenols, which consists of catalytic cracking of dihydroxydiarylalkanes in the presence of silica-alumina catalyst. In the present work, we investigated the catalytic cracking of 1,1-(4',4"-dihydroxy)diphenylethane, 1,1-(4',4"-dihydroxy-5',5"-dimethyl)diphenylethane, and 2,2-(4'4"-dihydroxy)diphenylpropane.

The cracking was carried out in a flow apparatus (Fig. 1). The solution of dihydroxydiphenylalkane in a suitable solvent was fed a constant rate by means of a piston pump from a graduated cylinder (4) into a tee, where it was mixed with steam from steam preheater (3). The resulting mixture was fed to reactor (2), which consisted of a quartz tube filled with quartz packing and catalyst. The temperature in the catalyst bed was measured with a chromel-alumel thermocouple and millivoltmeter, and was maintained constant within ±5°. The cracked products were collected in a receiver cooled by a stream of water. After separation of the water layer, the solution of cracked products in solvent was distilled in the presence of hydroquinone in a stream of nitrogen or without access of air, first at reduced pressure and then under vacuum for separation of the cracked products. The cracking catalysts used included a pelletted commercial silica-alumina catalyst and two silica-alumina catalysts containing 30 and 50% Al_2O_3.

Cracking of 1,1-(4',4"-dihydroxydiphenylethane. The 1,1-(4',4"-dihydroxy)diphenylethane was prepared



(1)

by alkylation of phenol with acetylene by a method we have previously described [6]; after recrystallization from benzene, the resulting white powder had an m. p. of 122.5°, and was readily soluble in alcohol, ether, acetone, and acetic acid and difficultly soluble in hydrocarbons.

The solvent used in the cracking process was a mixture of acetone, ether, phenol, or acetic acid with benzene; various dihydroxydiphenylethane feed rates were used with each of the different catalysts. The best results were obtained when the cracking was carried out in the presence of silica-alumina catalyst containing 50% Al_2O_3 using ether or acetic acid mixed with benzene as the solvent for the dihydroxydiphenylethane.

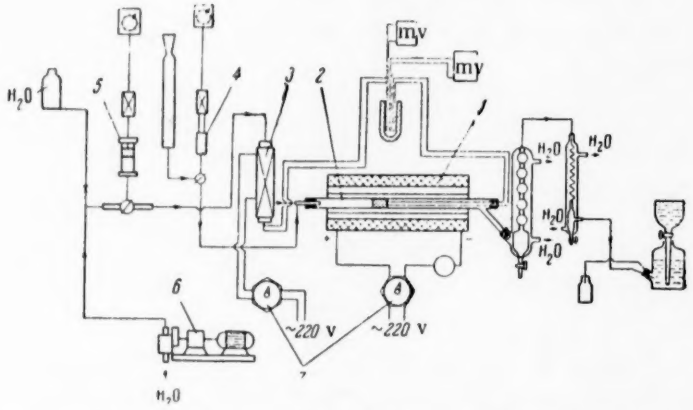


Fig. 1. Apparatus for the cracking of unsymmetrical diarylethanes. 1) Tubular furnace; 2) quartz reactor; 3) steam preheater; 4) raw feed; 5) water feed; 6) pump; 7) laboratory autotransformer.

In almost all cases, distillation of the cracking catalyzate yielded three fractions: Fraction I, phenol; Fraction II, phenol mixed with ethylphenol and p-vinylphenol; Fraction III, p-vinylphenol containing an insignificant amount of ethylphenol. When the cracking was carried out selectively and the concentration of p-vinylphenol in the cracked products was high, the p-vinylphenol usually crystallized out of Fraction III in the form of pale greenish leaves.

The yield of Fraction III and the conversion of the dihydroxydiphenylethane to lighter products increased with an increase in the space rate of the dihydroxydiphenylethane solution. A description of the most effective experiments on the cracking of dihydroxydiphenylethane is presented below.

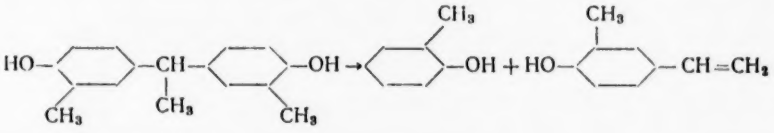
Water and a solution of 36 g of dihydroxydiphenylethane in 50 ml of ether and 70 ml of benzene were fed at rates of 4 ml/minute and 1 ml/minute (space rate of 2.4 hours^{-1}), respectively, to the reactor, which contained 25 ml of silica-alumina catalyst (about 50% Al_2O_3). The cracking temperature was 550°. The molar dilution of dihydroxydiphenylethane with steam and solvent (ratio of the number of moles of water and solvent to the number of moles of dihydroxydiphenylethane) was about 200. The contact time was 0.03 seconds. Distillation of the cracked products without access of air in a flask fitted with a 30-cm column yielded 11 g of a fraction boiling at 69-74°/3 mm (n_D^{20} 1.5498; mol. wt. 98; OH 18.4%), 2.5 g of a fraction boiling at 74-90°/3 mm (n_D^{20} 1.5632; mol. wt. 118; OH 14.2%), and 6.2 g (43.3% of theoretical) of a fraction boiling at 90-95°/3 mm (n_D^{20} 1.5789). The kettle residue (9.5 g) was unconverted dihydroxydiphenylethane. The fraction boiling at 90-95°/3 mm crystallized rapidly after distillation. After recrystallization and drying in a vacuum desiccator, the crystals were lustrous white leaves with an m. p. of 64-65°. After several recrystallizations of the product from benzene, the melting point became constant at 71.5-72°. The literature gives an m. p. of 73.5° for p-vinylphenol. The crude crystals of p-vinylphenol were readily soluble in benzene, alcohol, and ether, and were difficultly soluble in water; however, upon prolonged standing in a vacuum desiccator, the material became less soluble owing to polymerization. The p-vinylphenol crystals dissolved in basic solutions, imparting a brown color; when p-vinylphenol was added to concentrated sulfuric acid, the acid became bright red. When a solution of ferric chloride was added to an aqueous solution of p-vinylphenol, the solution became blue-green.

The p-vinylphenol rapidly polymerized to a white, insoluble resin when it was allowed to stand in air in the dark. However, it could be stored for 50 hours and longer under an atmosphere of inert gas. For identification

purposes, p-vinylphenyl allyl ether was prepared from the phenol by the method of reference [5]. The constants of the p-vinylphenyl allyl ether were: b. p., 81°/4 mm; n_D^{20} 1.5562. (literature values [5]: b. p. 82-83°/4 mm; n_D^{20} 1.5578). In addition to p-vinylphenol, we were also able to isolate from the cracking products and to identify phenol and ethylphenol (in the fractions boiling at 69-74°/3 mm and 74-90°/3 mm) and phenetole (in the fraction boiling at 69-74°/3 mm); the latter was present in small amounts. The formation of phenetole was a consequence of the reaction of a part of the diethyl ether with phenol during the cracking process. When the dihydroxydiphenylethane was cracked in solution in acetic acid and benzene, ether compounds were not found in the cracked products. The cracking was carried out under conditions analogous to those used when the solvent was ether and benzene.

Water and a solution of 30 g of dihydroxydiphenylethane in 15 ml of acetic acid and 20 ml of benzene were fed at rates of 10 ml/minute and 1 ml/minute, respectively, to the reactor, which contained 25 ml of silica-alumina catalyst (50% Al_2O_3). The molar dilution and the contact time were the same as in the preceeding experiment. The cracking temperature was 550°. Distillation of the catalyzate yielded 3 g of phenol as a fraction boiling at 68-74°/4 mm, 1.2 g of an intermediate fraction boiling at 74-88°/4 mm, and 5.2 g of p-vinylphenol as a fraction boiling at 88-102/4 mm (yield, 35.4% of theoretical).

Cracking of 1,1-(4',4"-dihydroxy-5',5"-dimethyl)diphenylethane. The 1,1-(4',4"-dihydroxy-5',5"-di-

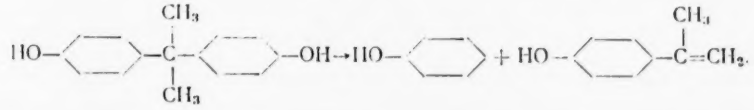


(2)

methyl)diphenylethane (ethylidene di-o-cresol) was prepared by alkylation of o-cresol with acetylene in alcohol solution [7]. This material was a white, crystalline substance with an m.p. of 89.5° and a b.p. of 206-210°/3 mm.

A solution of 30 g of ethylidene di-o-cresol in 20 ml of acetic acid and 90 ml of benzene was fed at a rate of 1 ml/minute to the reactor, which contained 25 ml of silica-alumina catalyst (about 50% Al_2O_3). Water was introduced at a rate of 4 ml/minute. The cracking temperature was 550°. The benzene was distilled from the catalyzate, and the latter was then distilled under vacuum in a Claisen flask in the presence of hydroquinone. The following fractions were obtained: 78-87°/4 mm, 6.8g; 87-98°/4 mm, 0.4 g; 98-110°/4 mm, 9.3 g. The kettle residue (10.4 g) was mainly unconverted ethylidene di-o-cresol. The fraction boiling at 78-87°/4 mm was o-cresol: mol. wt. 110; n_D^{20} 1.5483; OH 14.0% (literature data: n_D^{20} 1.5453; mol. wt. 108; OH 15.7%). The intermediate fraction, which boiled at 87-98°/4 mm, was apparently a mixture of o-cresol, 4-ethyl-o-cresol, and 4-vinyl-o-cresol: mol. wt. 136; n_D^{20} 1.5690; OH 13.8%. The fraction boiling at 98-110°/4 mm, 4-vinyl-o-cresol, solidified to a white crystalline substance with an m. p. of 73-74°; it was insoluble in the ordinary solvents, and readily transformed on standing in air to a tacky resin, treatment of which with benzene precipitated 4-vinyl-o-cresol polymer in the form of a white, insoluble powder.

Cracking of 2,2-(4',4"-dihydroxy)diphenylpropane. The 2,2-(4',4"-dihydroxy)diphenylpropane (diphenylol-



(3)

propane) used in the cracking experiments was GIPI-4 commercial product, obtained from the institute (State Design and Planning Scientific Research Institute), and was purified by distillation and recrystallization: b. p. 225-230°/8 mm, m. p. 157-159°.

A solution of 30 g of diphenylolpropane in 15 ml of acetone and 100 ml of benzene was cracked under conditions analogous to those described above. The catalyzate (25 g) was vacuum-distilled into the following fractions: 68-80°/4 mm, 4.8 g; 80-98°/4 mm, 6.2 g; and 98-108°/4 mm, 8.1 g. The kettle residue amounted to 5.3 g. The fraction boiling at 98-108°/4 mm crystallized to a yellow-green, crystalline mass. Recrystallization yielded white, lamellar crystals with an m. p. of 80.5°. Literature data for p-isopropenylphenol [5]: b. p. 125°/20 mm; m. p., 83-84°. When crystals of p-isopropenylphenol were allowed to stand in air, they were rapidly converted to a reddish resin, which was difficultly soluble in the ordinary organic solvents.

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CONTRIBUTION TO THE QUESTION OF THE CONNECTION BETWEEN THE CRYSTALLIZATION OF ALDEHYDES AND THEIR CONVERSION TO POLYOXYMETHYLENE-TYPE POLYMERS

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It is well known that thermally-stable high-molecular-weight polyoxymethylenes possessing valuable technical properties can be obtained from formaldehyde [1]. However, attempts to prepare analogous stable polymers from other aliphatic aldehydes have not been successful up to the present time. Nevertheless, very interesting data have been obtained during the course of these investigations, in particular, data having reference to the connection between the crystallization of acetaldehyde and the polymerization of this compound. Thus, it has been shown [2] that polymerization takes place at atmospheric pressure only concomitantly with melting of the acetaldehyde crystals. However, crystallization conditions have a decisive effect on the yield and properties of the polymer [3]. Acetaldehyde which has been carefully freed of oxygen (peroxides) and water does not polymerize; at the same time, when the content of water and alcohols exceeds a certain value, the reaction is substantially inhibited [4]. The polymer obtained in this manner is unstable even at temperatures close to room temperature, and, depending on the nature of the depolymerization initiator, can undergo depolymerization by either a radical or an ionic mechanism [5].

Several papers on the polymerization of butyraldehyde are available. This phenomenon was discovered by Bridgman and Conant [6], who obtained an unstable butyraldehyde polymer at room temperature and a pressure of 12,000 atm. The melting point of butyraldehyde at atmospheric pressure is −99°; therefore, it would seem very probable that crystallization of butyraldehyde would take place at a pressure of about 5000 atm. at room temperature. As a matter of fact, the melting points of benzene, nitrobenzene, bromoform, and a number of other compounds are 80-90° higher at a pressure of 4000 atm. than at atmospheric pressure. The major purpose of the present work was the clarification of the question of whether preliminary crystallization of butyraldehyde is required for its polymerization at high pressure.

EXPERIMENTAL

Purification of the butyraldehyde. One or two drops of concentrated H_2SO_4 and several pieces of $CaCl_2$ were added to the butyraldehyde, and the mixture was allowed to stand until the aldehyde was almost completely converted to parabutyraldehyde. The butyraldehyde was washed with water, dried over $CaCl_2$, and distilled under vacuum (b. p. 126-127/24 mm; n_D^{20} 1.4261, mol. wt. 207; mol. wt. calculated for $(C_4H_8O)_3$, 216. The parabutyraldehyde was placed in a Favorskii flask, concentrated H_2SO_4 (1 drop) was added, and the mixture was heated on a water bath in an atmosphere of nitrogen which had been freed of oxygen by passage, at 200°, through a tube of pyrophoric copper deposited on silica gel. The aldehyde which distilled contained up to 2% water.* In order to remove the water, the butyraldehyde was distilled in a column filled with glass packing and having an efficiency

*Approximate determination of the water content was carried out with Karl Fischer reagent.

of 15 theoretical plates; the distillation was carried out in an atmosphere of nitrogen. After distillation of the water–butyraldehyde azeotrope (b. p. 68.0°; 10.1% water [7]), the butyraldehyde was collected; b. p. 74.7-74.8°/760 mm; n_D^{20} 1.3792-1.3793; literature data [7]: b. p. 74, 78°/760 mm, n_D^{20} 1.37915. In a number of experiments, the butyraldehyde was dried with Drierite before distillation in the column [8, 9].

Experimental method. In order to investigate the question of whether preliminary crystallization is required for polymerization of butyraldehyde under pressure, experiments were carried out in a pressure intensifier fitted with two glass windows. The construction of the intensifier (Fig. 1) was similar to that of the intensifier described in reference [10]. The butyraldehyde was introduced into the channel of the high-pressure block 5 containing windows 6 and sample tube 7. Then oil was fed by a pump to the low-pressure section 1, and the force on piston 2 was transmitted through rod 3 to the mushroom-shaped bar 4, which, by moving, compressed the butyraldehyde. The apparatus was designed for a pressure of 8000 kg/sq. cm. at ordinary temperatures. The pressure in the channel of the high-pressure block was calculated from the pressure-multiplication factor (correction for friction was taken as 10% of the calculated pressure). During an experiment, a light source was fastened to one of the windows of the intensifier, and a photoelement was attached to the other window to measure the intensity of the transmitted light; the photoelement was connected to a mirror galvanometer.

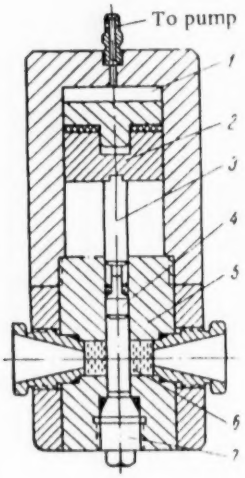

Fig. 1.

A series of experiments on the polymerization of butyraldehyde was carried out in an ordinary intensifier at a pressure of 7000 kg/sq. cm with a working volume of about 70 cc; the pressure was measured with a manometer having an upper limit of 10,000 kg/sq. cm. The butyraldehyde was charged by means of a syringe to a lead ampoule with a narrow outlet, which was then pressed together and sealed; the ampoule was then placed in the channel of the high-pressure block. The latter was filled with a mixture of glycerin and water (50%), and the required pressure was applied. Before the ampoule was filled, the syringe and ampoule were purged with purified nitrogen. Up to five ampoules could be charged to the intensifier. The solid polymer usually obtained was insoluble in acetone and alcohol; however, it was somewhat soluble in benzene, chloroform, and carbon tetrachloride. The amount of polymer formed was determined by weighing after the material had been washed with acetone and dried by passing air through it.

Results. In the work reported in reference [11], it was shown that butyraldehyde does not polymerize at 3000 atm. In order to determine the minimum pressure required for the formation of solid polymer, experiments were carried out in lead ampoules at higher pressures. This work showed that polymerization does not take place at 4200 kg/sq. cm. Thus, in one of the experiments, appreciable amounts of polymer had not formed after 19.5 hours at the indicated pressure. At 5200 kg/sq. cm. and the same time interval, several percent polymer was formed. An increase in the initial pressure to 6200-6300 kg/sq. cm. usually led to the formation of polymer with a yield of 40-80% after 17-20 hours. The addition of benzoyl peroxide significantly accelerated the process* at 6300 kg/sq. cm.; however, solid polymer was not formed in the presence of benzoyl peroxide at a pressure of 4200 kg/sq. cm. Thus, in the absence of an initiator, the yield of polymer was zero at 6300 kg/sq. cm. after two hours, while in the presence of 1.8% benzoyl peroxide, the yield was 73%; appreciable amounts of polymer were not obtained even after 67 hours at 4200 kg/sq. cm. in the presence of 2 and 3.7% benzoyl peroxide.

The data presented above show that a comparatively small increase in pressure (from 4200 to 5200 kg/sq. cm) bring about the formation of solid polymer. The question arises as to whether the polymerization of butyraldehyde is a consequence of crystallization and subsequent fusion of the butyraldehyde, as is the case in the polymerization of acetaldehyde. However, our attempts to polymerize butyraldehyde be repeated freezing and thawing at atmospheric pressure did not yield positive results. An investigation of the dependence of polymer yield on time at an initial pressure of 6300 kg/sq. cm. also indicated that polymerization is hardly connected with the instant at which fusion of the crystals occurs. Thus, in one experiment, the yield of polymer at 6300 kg/sq. cm. after 2, 4, and 18 hours was 0, 2.5, and 34.3%, respectively.

The most persuasive results were obtained in experiments carried out in the intensifier equipped with windows. In the first experiment, pure butyraldehyde was charged to the intensifier, and the pressure was

*The initiation of polymerization of butyraldehyde at 12,000 atm. by small amounts of oxygen and peroxides was first established in the work reported in references [12, 13].

brought to about 7000 kg/sq. cm. The intensity of the light transmitted through the material in the apparatus did not change over a period of 17 hours. When the material was removed, it was noticed that 3.5% polymer had formed in the lower part of the apparatus (in tube 7). This material was not present in front of the window; for this reason, and also as a consequence of the fact that crystallization of the aldehyde did not take place, the intensity of the transmitted light did not change with time. In the second experiment, butyraldehyde containing 2.8% benzoyl peroxide was charged to the intensifier. No material change in the light intensity was observed over the period of 2.5 hours following application of the pressure (7000 kg/sq. cm.). Another reading was taken after 17 hours; a sharp decrease in the intensity was then observed. The intensity of the transmitted light remained just as low after the pressure had been reduced to the minimum (about 100 kg/sq. cm.). The product removed from the apparatus contained 10 wt. % polymer (based on the butyraldehyde charged). If crystallization of the aldehyde had occurred during this experiment, the decrease in pressure would have brought about fusion of the aldehyde and, consequently, a decrease in the intensity of the transmitted light. For example, when benzene was compressed in the intensifier, a great decrease in the light intensity was observed at the instant the benzene crystallized under the influence of pressure. When the pressure was lowered, the intensity again increased to the initial value. These experiments indicate that butyraldehyde is capable of polymerizing under the influence of pressure without preliminary crystallization.

The effect of a number of initiators on the polymerization of butyraldehyde, and also on depolymerization of the solid polymers, was investigated during the course of our investigation. The experimental data obtained will be published separately. We shall note here only the basic results obtained during this investigation. The addition of about 1.3% water or of n-propyl alcohol (5%) to the butyraldehyde leads to a sharp decrease in the yield of solid polymer*. Hydroquinone (1.5-3%) is an inhibitor of the reaction. Azobisisobutyronitrile, in contrast to benzoyl peroxide, did not have an appreciable effect on the polymerization rate under the conditions studied. The polymers prepared at a pressure of 6300 kg/sq. cm. were white plastic materials which were unstable at atmospheric pressure. The addition to the polymer of hydroquinone or quinone (in quantities amounting to several weight per cent) stabilized the polymer, and made possible storage of the polymer exposed to air at room temperature for several months.

Discussion of results. The data presented above on the effect of initiators, water, and alcohol, have a definite similarity to the corresponding data obtained during the polymerization of acetaldehyde at atmospheric pressure and low temperature. At the same time, our experiments have shown that, in contrast to acetaldehyde, butyraldehyde can be polymerized to similar polymers without preliminary crystallization. In this connection, the report that it is possible to polymerize acetaldehyde over aluminum oxide at a temperature significantly exceeding the crystallization temperature of acetaldehyde [14] is deserving of attention. It is very interesting that butyraldehyde does not polymerize at 4200 kg/sq. cm., but can form solid polymers at a pressure of about 5200 kg/sq. cm., although it does not crystallize at this pressure. Possible causes of this phenomenon will be considered below.

One of the most important factors influencing the formation of solid butyraldehyde polymers under pressure is the shift of the equilibrium under the influence of pressure. Indeed, these polymers are unstable at atmospheric pressure, but they are formed in appreciable amounts at a pressure of about 5000 kg/sq. cm. Considering that the decrease in volume per mole of polymer formed is very large during polymerization (owing to the high molecular weight of the polymer), it is easy to arrive at the conclusion that a comparatively small increase in the pressure can lead to a very significant shift in the equilibrium of the polymerization reaction. Thus, for example, with a degree of polymerization of 50 and a decrease in the volume for each degree of polymerization (for example, upon conversion of monomer to dimer) of 10 cc/mole, the equilibrium constant, K_N, increases by a factor of 10^9 with an increase in the pressure of only 1000 kg/sq. cm.; such an increase in K_N corresponds to an increase in the equilibrium concentration of polymer from an initial 1 to 94 wt. %.

However, the question arises as to why polymerization begins to take place in the neighborhood of the pressure required for the crystallization of the aldehyde at room temperature. It is possible that the formation of butyraldehyde polymers proceeds under conditions such that the disposition of the molecules in the liquid is to a significant extent ordered, i.e., close to the crystallization point (see [15]). In this case, a substantial decrease in the negative value of the entropy of activation, i.e., a significant increase in the reaction rate, would be expected. Clarification of this question is the subject of further investigation in this laboratory.

* The formation of the unstable liquid polymer described in reference [11] was due to the presence of contaminating water in the monomer.

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*Original Russian pagination. See C. B. translation.

REARRANGEMENT OF α, α-DIFLUOROALKYL AZIDES

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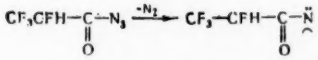
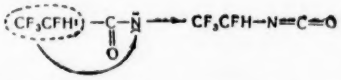
The well-known rearrangement of acid azides (the Curtius rearrangement), which leads to the formation of isocyanates, can be considered, in the light of contemporary theory, as a process of α-elimination from the nitrogen with the formation of nitrogen analogs of carbenes which may be called "azacarbenes"



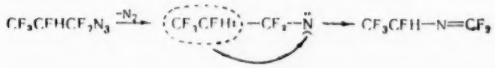
Azacarbenes stabilize in the form of isocyanates through the transfer of the radical with its pair of electrons to the electrophilic nitrogen:



β-Monohydroperfluoroalkyl azides, which may be prepared by the addition of hydrazoic acid to perfluoroolefins (see [1]), contain two atoms of fluorine in the alpha position to the azido group, and are unusual electronic analogs of acid azides:

$$R-CO-N_3, \quad R-CF_2-N_3.$$

Therefore, it would be expected that upon heating they would undergo a rearrangement similar to the Curtius rearrangement:



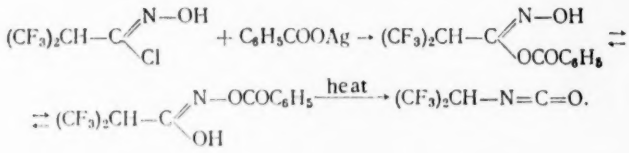
Indeed, when β-monohydroperfluoropropyl and β-monohydroperfluoroisobutyl fluorides were heated to 200°, the corresponding carbylamine fluorides were obtained. The structure of the carbylamine fluorides obtained by thermal rearrangement of α,α-difluoroalkylazides required proof.

The reaction of α-monohydroperfluoroisopropylcarbylamine fluoride with aniline gave a substituted urea which was identical with that obtained from α-monohydroperfluoroisopropyl isocyanate and aniline:

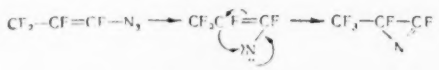
$$(CF_3)_2CH-N=CF_2 \xrightarrow[H_2O]{C_6H_5NH_2} (CF_3)_2CH-NH-CO-NHC_6H_5 \leftarrow \xrightarrow{C_6H_5NH_2} (CF_3)_2CH-N=C=O.$$

The reaction of perfluoroisobutylene with hydroxylamine [2] was used for the preparation of this isocyanate. The resulting fluoride of α-monohydroperfluoroisobutyrohydroxamic acid was converted by interaction with liquid hydrogen chloride to the chloride of this same acid; treatment of the latter with silver benzoate gave the benzoyl

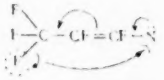
derivative of α-monohydroperfluoroisobutyrohydroxamic acid, which, upon being heated, underwent a Lossen rearrangement with the formation of α-monohydroperfluoroisopropyl isocyanate:



It would appear that the rearrangement of perfluoroalkenyl azides through the corresponding "perfluoroalkenylazacarbenes" should lead to compounds with a three-membered nitrogen-containing ring:



However, as reported previously [2], such "azacarbenes" in fact rearrange through the transfer of a fluorine from the γ-position to the nitrogen atom. It is probable that as a consequence of conjugation of the bonds in



such a rearrangement proceeds with considerably greater ease than does "unpairing" of the electrons of the π-bond, the electron density of which is lowered.

EXPERIMENTAL

1. α-Monohydroperfluoroisopropylcarbylamine fluoride. Through a glass tube, heated to 205-210° by a tubular electric furnace, was passed 4.7 g of 2-monohydroperfluoroisobutyl azide. The pyrolysis product was collected in a trap cooled with solid carbon dioxide. The 2-monohydroperfluoroisopropylcarbylamine fluoride was separated by distillation. This was a colorless liquid with the odor of phosgene; b. p. 36°, d_4^{20} 1.5350; n_D < 1.3. Mol. wt.: found, 221; calculated for C_4HF_8N, 215. F: found, 70.50%; calculated, 70.70%.

A weighed sample of this carbylamine fluoride was dissolved in aniline water, heated for 5 minutes, and the fluorine titrated. F: found, 17.85%; theoretical for two fluorine atoms, 17.70%.

2. α-Monohydroperfluoroethylcarbylamine fluoride. The pyrolysis was carried out in the manner described for Experiment 1. The 2-monohydroperfluoroethylcarbylamine fluoride was a colorless liquid with a b. p. of 24°, d_4^0 1.5000. Mol. wt.: found, 167; calculated for C_3F_6HN, 165. F: found, 68.74%; calculated, 69.09%. A weighed sample of this carbylamine fluoride was dissolved in aniline water, heated for 5 minutes, and the fluorine titrated. F found, 11.30%; theoretical for two F atoms, 11.51%.

3. Phenylhexafluoroisopropylurea. An ether solution of aniline was added to 0.5 g of α-monohydroperfluoroisopropylcarbylamine fluoride. The reaction was exothermic. The ether was distilled, and the residual tacky crystalline mass wasrecrystallized from aqueous alcohol. The m. p. was 210° (after two recrystallizations). A mixture of this material with a known sample of $(CF_3)_2CHNHCONHC_6H_5$ showed no depression of the melting point.

Found %: C 42.08; H 2.70; N 9.68. Calculated %for $C_{10}H_8F_6N_2O$: C 41.96; H 2.80; N 9.89.

4. Chloride of α-monohydroperfluoroisobutyrohydroxamic acid. Into a steel test tube was introduced, with cooling, 22.5 g of an ether complex of α-monohydroperfluoroisobutyrohydroxamyl fluoride and 25 ml of liquid hydrogen chloride. The contents of the test tube were agitated on a shaker at room temperature for 3 hours; the test tube was then cooled, opened, and slowly brought to room temperature. The contents of the test tube were transferred to a separatory funnel containing ether and washed several times with small portions of water until the water layer became clear. The ether layer was separated, dried over calcium chloride, and distilled. The α-monohydroperfluoroisobutyrohydroxamyl chloride was a colorless liquid with a sharp odor. The b. p. (after a second distillation) was 58° at 38 mm, d_4^{20} 1.4780; n_D^{20} 1.3570.

Found %: C 24.88; H 1.83; N 5.67; F 45.70; Cl 14.15. Calculated % for $\left[(CF_3)_2CHC\begin{matrix}Cl\\ \diagdown\\ \diagup\\ NOH\end{matrix}\right]_4(C_2H_5)_2O$.

C 24.15; H 1.82; N 5.77; F 45.97; Cl 14.32.

5. Benzoyl derivative of α-monohydroperfluoroisobutyrohydroxamic acid. Ten grams of α-monohydroperfluoroisobutyrohydroxamly chloride was added to a suspension of 27.6 g of silver benzoate in 50 ml of dry ether.

The reaction mixture was stirred for two days at room temperature. The precipitate was then filtered off, and the filtrate was distilled. The crystals remaining after distillation of the ether had an m. p. of 175° (aqueous alcohol).

Found %: F 34.92; N 4.56. Calculated % for $C_{10}H_5OF_6N_2$: 36.18; N 4.44.

6. Phenylhexafluoroisopropylurea. In a round-bottom flask fitted with a reflux condenser were placed 3 g of the benzoyl derivative of α-monohydroperfluoroisobutyrohydroxamic acid and 10 ml of nitrobenzene. The end of the condenser was connected to a receiver submerged in a cooling mixture contained in a Dewar. The flask was heated at the boiling point of the nitrobenzene. Liquid collected in the receiver; when aniline was added to the liquid, white crystals precipitated. These had an m. p. of 211° after recrystallization from aqueous alcohol.

Found %: C 42.08; H 2.89; F 39.50; N 9.54. Calculated % for $C_{10}H_5OF_6N_2$: C 41.96; H 2.80; F 39.86; N 9.89.

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*Original Russian pagination. See C. B. translation.

THE PREPARATION OF NEW TYPES OF LINEAR POLYMERS BY POLYRECOMBINATION REACTIONS

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In previous investigations relating to the study of polyrecombination reactions [1, 2], it was shown that when such compounds as p-diisopropylbenzene, diisopropylferrocene, p-dichlorobenzene, p-xylylene dichloride, and a number of others are treated with peroxides, linear polymers are formed, and, in addition, there is obtained (particularly in the case of p-diisopropylbenzene) a significant amount of polymers with a cross-linked three-dimensional structure, which are ordinarily infusible and insoluble. In the course of further investigations, we have studied the behavior in polyrecombination reactions of such compounds as diphenylmethane and some of its derivatives, the methyl ether of phenylacetic acid, and benzyl benzoate, from which only the dimers have previously been prepared by treatment with peroxides [3, 10].

Polymers without any appreciable amount of three-dimensional structure were obtained when these compounds and a number of others were treated, by the method previously described [2], with tert-butyl peroxide, at a ratio of 1.2 or more moles of peroxide per mole of the original compound; the reaction temperature was 200°. Thus, a linear polymer was obtained from diphenylmethane; the polymer was a yellowish powder with an m. p. of 205-220°, and was soluble in benzene. The molecular weight of this polymer varied within the limits of 10,000 to 900,000 depending on the mole ratio of peroxide to hydrocarbon. The relationship of the molecular weight of this polymer and the viscosity of its benzene solution is well expressed by the formula $[\eta] = 2.18 \cdot 10^{-3} M^{0.328}$.

Formation of the polymer can be represented by the following scheme:

$$(C_6H_5)_2CH_2 + R\cdot \rightarrow RH + (C_6H_5)_2\dot{C}H;\ 2(C_6H_5)_2\dot{C}H \rightarrow HC(C_6H_5)_2CH(C_6H_5)_2 \xrightarrow{R^{\cdot}} \rightarrow HC(C_6H_5)_2C^{\cdot}(C_6H_5)_2 \rightarrow HC(C_6H_5)_2C(C_6H_5)_2C(C_6H_5)_2 - \cdots - CH(C_6H_5)_2, \quad (I)$$

where $R^{\cdot}$ – is tert-butoxy and methyl radicals, which are formed by decomposition of the peroxide [7, 8]:

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO\cdot \rightarrow (CH_3)_3CO\cdot + \cdot CH_3 + (CH_3)_2CO.$$

Thus, this polymer can be considered as a polydiphenylmethylene (I), which was previously unknown, since it cannot be prepared, for example, from tetraphenylethylene under mild polymerization conditions (see reference [4]). By analogy with hexaphenylethane and higher completely arylated paraffins [5], it would be expected that a polymer having such a structure would be unstable and would have a tendency toward spontaneous dissociation.

As a matter of fact, this polymer did not show any signs of decomposition into free radicals in the presence of diphenylpicrylhydrazine, and it also exhibited considerable stability toward the action of such oxidizing agents as nitric acid and chromic acid. It is quite probable that the stability of the polymer is associated with the fact that the first product of the polyrecombination reaction – the dimer, tetraphenylethane – is, in

in contrast to hexaphenylethane, an entirely stable compound [5]. Dissociation of tetraphenylethane and its high-molecular weight analogs is not stimulated by the formation of triphenylmethyl radicals, as occurs in the case of hexaphenylethane and higher completely arylated alkanes.

Other explanations of the stability of the polymer involve: a) the assumption of a rearrangement of the benzene rings during the course of the reaction in a manner similar to the Gomberg rearrangement [11]; this would lead to the structure of a poly-α,α,α'-triphenylxylylene (II), the stability of which is due to the presence of phenyl groups joined to the main chain in the 1 and 4 positions; b) the assumption of a rearrangement similar to that observed by Ziegler for 1,2-dimethyltetraphenylethane [12]. As applied to our case, this scheme should lead to the formation of an unsymmetrical diphenylethylene and subsequent polymerization of this compound with the formation of polydiphenylethylene (III).

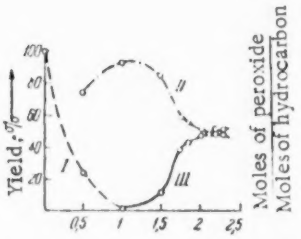


Fig. 1. Dependence of the yield of diphenylmethane polymer and dimer on the mole ratio of peroxide to hydrocarbon. I) Original hydrocarbon; II) dimer; III) polymer.

The percentage composition of the elemental unit is the same for structures (I) and (II), $(C_{13}H_{10})_x$ (C, 93.93%; H, 6.07%); the unit in (III) has the composition $C_{14}H_{12}$ (C, 93.28%; H, 6.72%). The products of the oxidation of structures (I) and (III) should be the same. In order to resolve the question of which structure should be assigned to our polymer, a comparison was made of the infrared spectra of polymers prepared under the same conditions from different starting compounds, specifically, from diphenylmethane, tetraphenylethane, tetraphenylethylene, and 1,1-diphenylethylene. When the comparison was made, structure (II) was immediately dropped, since the infrared spectrum of polydiphenylmethylene showed no absorption maximum in the region of 833-840 cm^{-1}, which is characteristic of a benzene substituted in the 1 and 4 positions.

On the other hand, the spectra of the polymers prepared from diphenylmethane and tetraphenylethane had coinciding absorption maxima in the region of 701 and 747 cm^{-1}, which is characteristic of monosubstituted benzene [6], but they did not have a maximum in the region of 760 cm^{-1}, which was clearly apparent on the spectrum of the polymer prepared from 1,1-diphenylethylene. This maximum is characteristic of the configuration $C_6H_5-\underset{|}{\overset{|}{C}}-CH_2-$, which contains a methylene group and which is encountered in polymers prepared from dibenzyl, styrene, and 1,1-diphenylethylene. Thus, on the basis of the infrared data, structure (I) – polydiphenylmethylene – must be assigned to the polymer obtained from diphenylmethane.

Figure 1 presents the relationship between the yield of reaction products and the mole ratio of peroxide to hydrocarbon. It is apparent from this figure that the first mole of peroxide is consumed almost exclusively in the conversion of all of the diphenylmethane to the dimer, tetraphenylethane, the yield of which was >90% (Curve II). During the course of the reaction, the tetraphenylethane was not completely converted to polymeric products; its yield decreased to 50% (at a mole ratio of peroxide to hydrocarbon of 2:1) and then remained constant with the further addition of peroxide, as did the yield of polymer which reached 50% at this same ratio (Curve III). This stabilization of the polymer and dimer yields was apparently connected with the change in the viscosity of the medium which, toward the end of the reaction, was not a solution but a viscous mass. The increase in the viscosity of the medium hindered the release of radicals from the cells [13].

It may be seen from Fig. 2 that the addition of peroxide above two moles per mole of diphenylmethane led to a sharp increase in the molecular weight of the polymer (Curve II asymptotically approaches the ordinate axis), which reacted a maximum value of 900,000 (determined by light scattering).

In Fig. 2, Curve I is the theoretical curve of the change in the molecular weight of the polymer with changes in the mole ratio of peroxide to hydrocarbon. This curve was constructed on the basis of the assumption that the chain length increased by doubling of the chain; i.e., tetramer is formed from dimer, octamer is formed from tetramer, etc. On the basis of this assumption, the number of moles of free radicals required for the conversion of one mole of hydrocarbon to polymer with an infinite molecular weight can be expressed by the equation: $N_R = 1 + {}^1/_2 + {}^1/_4 + \ldots + ({}^1/_2)^k$, where k is an integer of the series 0, 1, 2, . . .; i.e., the number of moles can be expressed as the sum of a geometric progression in which the first member $a = 1$ and the common ratio $q = {}^1/_2$.

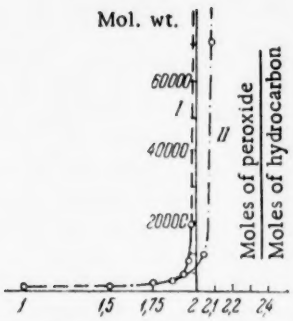


Fig. 2. Dependence of the molecular weight of the polymer on the mole ratio of peroxide to hydrocarbon. I) Theoretical curve; II) experimental curve.

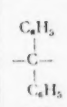
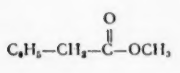
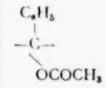
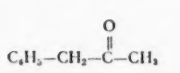
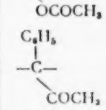
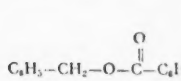
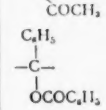
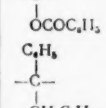
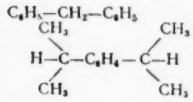
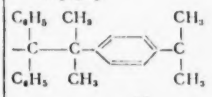
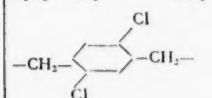
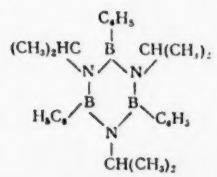
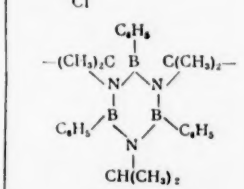
On the other hand, according to the above assumption, the polymerization coefficient $n = 2^{k+1}$. Hence, we obtain the following relationship between the number of moles and the coefficient n: $N_R = 2 - 2/n$.

It may be seen from Fig. 2 that the experimental curve II has precisely the same shape as the theoretical curve I, and agrees with it rather closely, which confirms the assumption made as to the method by which the chain increases.

From this it follows that, under the experimental conditions employed, tert-butyl peroxide decomposes in a manner such that one mole of peroxide yields not two moles of radicals which are active with respect to the solvent [8, 9], but one mole of such radicals, and, correspondingly, the maximum molecular weight is reached at a peroxide consumption close to two moles per mole of hydrocarbon. This can be explained on the basis that half of the initially formed free radicals is consumed, under these conditions, not by extracting hydrogen atoms from the solvent, but by side reactions. Methane in an amount of 50% of theoretical was detected in the gaseous products by gas chromatography. The corresponding loss of methyl radicals can be

TABLE 1

Compounds Which Undergo Polyrecombination to Yield Linear Polymers

Original compound	Mole ratio of peroxide to orig. comp.	Structural unit of the linear polymer	Mol. wt.	M.p., °C	Yield, % of orig. comp.
$C_6H_5-CH_2-C_6H_5$	2,3 : 1		900 000	205—220	52
	2,5 : 1		14 000	160—170	48
	1,86 : 1		30 000	210—220	36
	2,7 : 1		430 000	185—200	55
$C_6H_5-CH_2-CH_2-C_6H_5$	3 : 1		5 000	170—185	70
	2,5 : 1		23 000	146—160	55
$C_6H_4(CH_3)_2Cl_2$	2 : 1		10 000	150—165	65
	2 : 1		Trimer	~200	49
	1 : 1		2500	~300	16

partially explained on the basis that in addition to the decomposition of butoxy radicals into methyl radicals and acetone, reaction of these radicals among themselves takes place with the formation of methyl tert-butyl ether and acetone [14].

Linear, benzene-soluble polymers of high molecular weight were prepared in a similar manner from methyl phenylacetate, benzyl benzoate, and other compounds, which are shown in Table 1. In contrast to the linear polymers described above, when durene, ditolylmethane, p,p'-diisopropylbiphenyl, benzyl acetate, and certain other compounds were reacted instead of diphenylmethane, in addition to linear polymers significant amounts of insoluble polymers were formed; these apparently had a structure cross-linked through the methyl groups. It is interesting that linear polymers with aromatic rings not only in the side chains but also in the main chain can be prepared by polyrecombination reactions. Thus, for example, copolymerization of diphenylmethane (0.1 mole) and p-diisopropylbenzene (0.1 mole) in the presence of 2.5 moles of peroxide gave linear polymer exclusively, while p-diisopropylbenzene alone is converted under these conditions almost completely to a three-dimensional product [2]. Under these same conditions, 2,5-dichloro-p-xylene gave the chlorinated analog of poly-p-xylylene, which is completely soluble in benzene. Apparently, chlorine atoms in positions ortho to the methyl groups screen them and hinder cross-linking of the linear chains through these groups.

From the data presented above, it follows that polyrecombination leads to the formation of linear polymers of high molecular weight if the original compounds contain no groups which can serve as points of branching of the polymer chain.

If both of the benzene rings of diphenylmethane have electron accepting carbomethoxy groups (dimethyl p,p'-diphenylmethanedicarboxylate), then, in contrast to the case of diphenylmethane, the polyrecombination reaction is limited to the stage of dimer formation, which may be associated with, in addition to other factors, the greater difficulty with which α-hydrogen atoms are removed when electron accepting substituents are present in the ring. Dimer having the indicated structure was isolated with a yield of 75.6 %.

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ON CERTAIN CASES OF RADICAL-REDISTRIBUTION REACTIONS OF LEAD, TIN, AND SILICON ORGANIC COMPOUNDS

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It is well known that heating an unsymmetrical organometallic compound of the type $R_3R'Pb$ with a catalytic amount of aluminum chloride leads to redistribution of the radicals [1]. This results in the establishment of a dynamic equilibrium and the formation of a mixture of all possible combinations of tetraalkyl derivatives of the corresponding metal.

It seemed of interest to investigate this reaction for the case where the equilibrium state is disturbed so that the ratios between the reaction products differ sharply from those usually observed. It seemed to us that such a case would be the disproportionation of hexaethyldiplumbane and hexaethyldistannane under the influence of catalytic amounts of aluminum chloride and similar substances.

It is known that redistribution of radicals in a symmetrical compound of the type of tetraethyllead does not result in the formation of new substances. Consequently, the very fact that hexaethyldimetals change under the influence of a catalyst indicates that they are "unsymmetrical." Such a conclusion is correct, since any of the metal atoms in these compounds is joined to three ethyl radicals and one triethylmetal radical, for example: $(C_2H_5)_3SnR$, where R is $(C_2H_5)_3Sn$.

If it is assumed that each species of radical equally readily participates in redistribution reactions, then, according to the information in the literature, a mixture of the following compounds should be formed during the course of the reaction: $(C_2H_5)_4Sn$ (I), $(C_2H_5)_3SnR$ (II), $(C_2H_5)_2SnR_2$ (III), $C_2H_5SnR_3$ (IV), and SnR_4 (V).

It is readily apparent that even this basic reaction leads to the formation of rather complex molecules, since in compounds (III), (IV), and (V) there are chains of three, four, and five metal atoms, respectively.

However, in contrast to the case of classical redistribution reactions, this mixture is not an equilibrium mixture, since (III), (IV), and (V) are not "symmetrical" compounds. Thus, for example, (III) can be considered as $(C_2H_5)_3SnR'$, where R' is $(C_2H_5)_2Sn-Sn(C_2H_5)_3$. Consequently, theoretically it is probable that (III), (IV), and (V) enter into side reactions involving the redistribution of radicals, during the course of which, in addition to tetraethyltin, there are formed a series of substances with longer and more branched chains of metal atoms. An additional reason that the mixture of compounds (I)-(V) will not be an equilibrium mixture is that in addition to the formation of more complex molecules, these more complex molecules decompose, since chains of metal atoms are very unstable. In the case of organolead compounds, even a substance of the type of (III) should be extremely unstable, even at room temperature:

$$(C_2H_5)_3Pb-\underset{\displaystyle C_2H_5}{\overset{\displaystyle C_2H_5}{\underset{|}{\overset{|}{Pb}}}}-Pb(C_2H_5)_3 \rightarrow 2(C_2H_5)_4Pb + Pb. \qquad \text{(A)}$$

In the case of organotin compounds, the formation of longer or shorter chains of tin atoms is possible, the length depending on the temperature conditions. However, in this case decomposition of the complicated molecules with liberation of the metal should be observed at comparatively low temperatures.

In agreement with the ideas indicated above, it has been found that when 2-3 wt. % aluminum chloride or other radical-distribution catalyst (triethyllead bromide, diethyllead dibromide) is introduced into hexaethyldiplumbane, the stability of this compound is sharply decreased, and the mechanism of the decomposition changes.

Thus, for example, pure hexaethyldiplumbane decomposes completely in five hours at 105° in the absence of air [2]:

$$(C_2H_5)_6Pb_2 \rightarrow (C_2H_5)_4Pb + Pb + 2C_2H_5. \qquad (B)$$

This same compound disproportionates completely in 2-3 hours in the presence of 1.0-1.5% $AlCl_3$ at room temperature in accordance with the equation:

$$2(C_2H_5)_6Pb_2 \rightarrow 3(C_2H_5)_4Pb + Pb. \qquad (C)$$

The addition of aluminum chloride to hexaethyldistannane has a similar effect. In this case, the pure compound begins to decompose in accordance with Equation (B) at temperatures of 260-265°. Disproportionation of this compound in accordance with Equation (C) is observed at temperatures as low as 70-75° in the presence of a catalyst (2-3%).

We have shown, by means of spectrophotometry, that the decomposition of hexaethyldiplumbane [2] and of hexaethyldistannane takes place in accordance with Equation (B) with the intermediate formation of diethyllead or diethyltin. We were unable to demonstrate the presence of intermediate reaction products during the disproportionation of hexaethyldiplumbane according to Equation (C). On the other hand, the formation of intermediate products during the disproportionation of hexaethyldistannane under mild conditions (70-75°) is established by the appearance of an intense cherry red color and subsequent stratification of the reaction mixture. Analysis of the upper, colorless layer showed that it consists chiefly of tetraethyltin. Analysis of the remaining heavy, viscous, dark red liquid showed that it has the same composition as diethyltin: $[Sn(C_2H_5)_2]n$. Analysis for chlorine established that the catalyst was equally distributed between the upper and lower layers.

It should be emphasized that the phenomenon of stratification has nothing in common with tar formation, since decomposition of the lower layer with the formation of metallic tin and tetraethyltin was observed after stratification. Both the analytical data and the fact that stratification occurred indicates that high-molecular-weight intermediate substances are formed during the course of the disproportionation of hexaethyldistannane under the influence of $AlCl_3$; this is in agreement with the ideas presented above relative to the mechanism of this reaction.

In the case under consideration, disturbance of the equilibrium state proceeds through the participation of the reaction products in side processes leading to the formation of unstable compounds. There is a second possibility – when one or several of the reaction products is unstable toward the action of the catalyst.

In was established in 1934 that exchange of an ethyl radical for a chlorine atom takes place between $(C_2H_5)_4Pb$ and $(C_2H_5)_3PbCl$ [3]. It was shown that equilibrium is established after one day and that triethyllead chloride itself is a catalyst for the process.

It is natural to assume that this same exchange process, but without the formation of an equilibrium mixture, should take place during the interaction of tetraethyl derivatives of lead, tin, and silicon with alkyl halides in the presence of small amounts of catalysts for the redistribution of radicals. For example:

$$R_4Sn + R'Cl \xrightarrow[AlCl_3]{2-3\%} R_3SnCl + R-R'. \qquad (D)$$

The possibility of such processes followed from the work of Skoldinov and Kocheshkov [4] on the interaction of tetraphenyl- and tetraethyltin with acyl chlorides and with carbon tetrachloride and also from the work of Russell [5] on the dealkylation of tetraethylsilane by methyl bromide. In both cases, the authors used equimolar amounts of the halogen derivative and aluminum chloride.

We found that the rapid addition of 0.1 mole of dry isopropyl chloride to a mixture of 0.1 mole of tetraethylsilane and 0.3 g of $AlCl_3$ causes a spontaneous reaction. Additional refluxing of the mixture for 2 hours led to the formation of triethylchlorosilane. The yield was 71.3% of theoretical. B. p. 143-145°; n_D^{20} 1.4316. The reaction proceeds smoothly, and it may be used for preparational purposes. The structure of the triethylchlorosilane was confirmed by conversion to hexaethyldisilane [6].

The interaction of tetraethyltin with benzyl chloride proceeded just as vigorously. In this case, a side reaction involving condensation of the benzyl chloride takes place under the influence of the aluminum chloride, even under mild conditions [7]. Interaction of isopropyl chloride with tetraethyltin, hexaethyldistannane, and triethyltin chloride was successful only in the presence of small amounts of benzene as a solvent, which is known to accelerate reactions of a similar type [8]. In the case of hexaethyldistannane, disproportionation according to Equation (B) takes place along with the exchange process. It was not possible to carry out the exchange reaction between isopropyl chloride and tetraethyllead. The experimental results are presented in Table 1.

TABLE 1

Expt. No.	Taken for the reaction				Isolated from the reaction				
	organotin comp., moles	alkyl halide, moles	benzene, ml	$AlCl_3$, g	substance	b.p., °C	n_D^{20}	m.p., °C	yield, %
1	$(C_2H_5)_4Sn$, 0.10	iso-C_3H_7Cl, 0.10		0.28	$(C_2H_5)_4Sn$	175—176	1.4728	—	—
2	$(C_2H_5)_4Sn$, 0.05	iso-C_3H_7Cl, 0.05	1.9	0.160	$(C_2H_5)_3SnCl$	203—208	1.5035	—	68.3
3	$(C_2H_5)_4Sn$, 0.05	$C_6H_5CH_2Cl$, 0.05		0.22	$(C_2H_5)_3SnCl$	204—210	1.5043	—	73.0
4	$(C_2H_5)_4Sn$, 0.02	CCl_4, 0.02		0.50	$(C_2H_5)_3SnCl$	205—208	1.5047	—	53.6
					$(C_2H_5)_2SnCl_2$	—	—	83—84	10.0
5	$(C_2H_5)_4Sn$, 0.05	iso-C_3H_7Cl, 0.10	1.9	0.31	$(C_2H_5)_3SnCl$	204—210	—	—	54.8
					$(C_2H_5)_2SnCl_2$	—	—	82—83	31.4
6	$(C_2H_5)_3SnCl$ 0.05	iso-C_3H_7Cl, 0.05	2.0	0.25	$(C_2H_5)_2SnCl_2$	—	—	82—83	35.5
7	$(C_2H_5)_4Sn_2$, 0.019	iso-C_3H_7Cl, 0.019	1.0	0.14	$(C_2H_5)_3SnCl$	203—209	1.5039		55.5
					$(C_2H_5)_4Sn$	175—178	1.4743		22.5

Note. Reaction conditions: Nos. 1, 2, 5, and 6, heated at the boiling point for 2-3 hours; No. 4, heated in an evacuated ampoule on a boiling water bath for 16 hours; No. 7, heated in an evacuated ampoule at 70-80° for 48 hours; No. 3, the $C_6H_5CH_2Cl$ was added dropwise to the cooled aqueous mixture, and the mixture was then stored at room temperature for 12 hours.

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THE STRUCTURE AND CATALYTIC PROPERTIES OF CHROMIA-SILICA GEL CATALYSTS

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In the majority of cases, the dehydrogenation and dehydrocyclization action of Cr_2O_3 have been investigated using chromia-alumina catalysts. However, the possibility of using silica gel as a carrier for Cr_2O_3 has repeatedly attracted the attention of investigators [1-3].

During a study of the aromatization of paraffinic hydrocarbons over different catalysts, including chromia-silica gel, we noted that one of the species of catalysts, specifically chromia-silica gel, when given a preliminary treatment with ethyl alcohol exhibited a considerable change in stability during the aromatization of n-heptane, the stability depending on the nature of the gas in which the fresh catalyst was heated prior to the experiment. This circumstance prompted us to undertake a more detailed study of the effect of the method of preparation on the dehydrogenation activity and structural characteristics of these catalysts in the hope of shedding some light on the factors influencing the stability of oxide catalysts during dehydrocyclization.

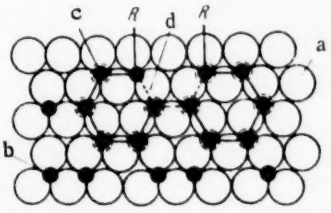


Fig. 1. Adsorption of a paraffinic hydrocarbon on crystalline Cr_2O_3 (Plane III): a) O^{2-} ions; b) Cr^{3+} ions; c) C atoms; d) possible sites of bond formation.

It was found that a chromia-silica gel catalyst which had been given a preliminary treatment with alcohol and heated to the temperature of the experiment in a stream of air was rapidly poisoned during the dehydrocyclization of heptane, possessed antiferromagnetic properties, and gave an x-ray pattern which contained Cr_2O_3 lines. This same catalyst preparation when reduced with alcohol but heated prior to the experiment in a stream of hydrogen was hardly poisoned during the course of two experiments on the aromatization of n-heptane, was paramagnetic, and gave an x-ray pattern which was characteristic of an amorphous substance.

On the basis of these differences in the structural characteristics of these two catalysts, reasons may be proposed to account for the difference in certain of their catalytic properties, particularly the difference in stability during the experiments. It has been proposed that aromatization of paraffinic hydrocarbons proceeds by a doublet-sextet mechanism [4, 5], which requires a specific spatial distribution of the chromium atoms in the form of sextets [4-6]. The antiferromagnetism of the first sample is associated with the presence of crystalline Cr_2O_3, in which each Cr^{3+} ion (in a given plane) is surrounded by three other Cr^{3+} ions having opposite total spins, and they all form a continuous network of sextets in Plane III [6]. Paraffin molecules falling on two neighbor-

ing sextets of Cr^{3+} ions can adsorb in a manner (see Fig. 1) such that, in addition to intramolecular C–C bond formation leading to aromatization of the paraffinic hydrocarbon, the formation of intermolecular C–C bonds becomes possible, which would lead to the creation on the surface of the catalyst of a small chain or network of hydrocarbon molecules (i.e., polymer) which is converted to coke.

The paramagnetic properties of the second sample indicate the absence of antiferromagnetic interaction. This could be connected with a distribution of Cr^{3+} ions such that the sextets do not form a continuous network, but are scattered over the surface of the carrier. As a consequence, the formation of intermolecular C–C bonds leading to the deposition of coke is greatly inhibited.

Since poisoning of the catalyst during an aromatization experiment is caused by deposition of coke on the catalyst surface, the differences in the catalyst structures noted above must have an effect on catalyst stability during an experiment, as was found experimentally.

EXPERIMENTAL

The experiments were carried out by a method described previously [7]. Catalyst 1 was prepared from KSK [Soviet Control Commission] large-pore silica gel after treatment to remove completely Cl and SO_4 ions. The silica gel, dried by heating at 110°, was impregnated with an aqueous CrO_3 solution in an amount calculated to yield 15 mole % Cr_2O_3 in the final catalyst. The catalyst was dried and then reduced with ethyl alcohol. A sample of the catalyst (20 cc) was heated to 535° in a stream of air (Catalyst 1A) and then used in an experiment with heptane. The yield of aromatics was 35 wt. %. The initial catalyst activity was high, but the catalyst was rapidly poisoned during the course of the experiment (see Fig. 2). At the same time, its activity for dehydrogenation of cyclohexane was almost unchanged during a two-hour experiment. Upon regeneration, the catalyst almost completely recovered its initial activity, and was again rapidly poisoned during the course of the experiment.

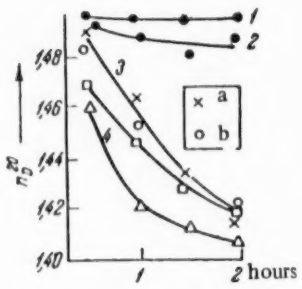


Fig. 2. Change in the index of refraction of the catalyzates during the course of the experiment: 1) Catalyst 1B heated in a stream of H_2; 2) catalyst 2B heated in a stream of H_2; 3) catalyst 1A heated in a stream of air [a) fresh catalyst, b) after regeneration]; 4) catalyst 1B after regeneration; 5)* catalyst 2A heated in a stream of air.

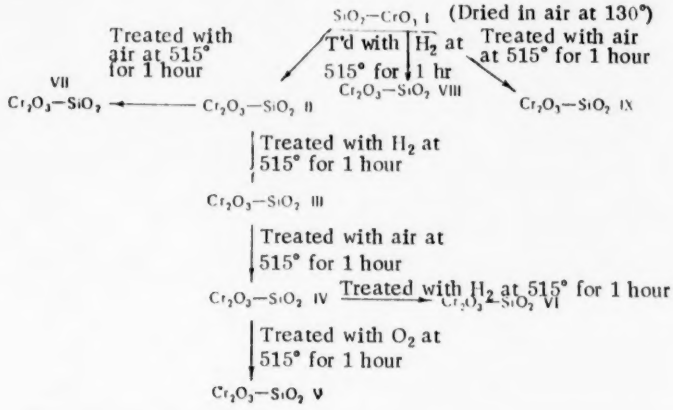
Catalyst 1B (which was treated with ethyl alcohol, dried, and heated to the temperature of the experiment in a stream of hydrogen) behaved differently than the preceding catalyst. The yield of aromatics with a fresh sample of Catalyst 1B was 56%. The catalyst lost almost no activity during the course of a two-hour experiment, as may be seen from the small change in refractive index of the catalyzate with time (see Fig. 2). After the first regeneration with air, the activity of Catalyst 1B decreased, and it rapidly became poisoned during the experiment, so that the yield of aromatics in the experiment following the regeneration and in succeeding experiments was approximately 35%.

Thus, heating of the individual samples of Catalyst 1 in a stream of air led in all cases to a decrease in the stability of the catalyst during dehydrocyclization. Further experiments were carried out to determine the reason for this phenomenon.

First of all, Catalysts 2A and 2B were prepared in a manner similar to that used for Catalysts 1A and 1B but using a silica gel from which the metal oxides had been removed by repeated boiling with fresh portions of concentrated HCl and subsequent washing with HCl, HNO_3, and water. As may be seen from the data in Table 1, the difference in the behavior of Catalysts 2A and 2B was analogous to that observed with Catalysts 1A and 1B. It was thereby established that the difference in the properties of catalysts given a preliminary heating in a stream of air or H_2 did not depend on metal oxide impurities contained in the silica gel. Inasmuch as the CrO_3 was carefully purified by recrystallization, it may be assumed that the difference observed in the behavior of the catalysts was due to differences in their structure and phase composition caused by their different history. Therefore, we investigated the effect of the method of preparation on these catalyst properties by x-ray and magnetochemical methods using a series of preparations of Catalyst 2 (for convenience, the different samples will be numbered with Roman numerals); conditions used for the preparations of these

* Not labelled in Russian diagram – Publisher's note.

catalysts are indicated in the scheme below. The magnetic susceptibility of the paramagnetic samples was determined by the Faraday method over the temperature range of 20-160° and a field strength of 3000 to 5000 oersteds, and the magnetic susceptibility of the diamagnetic samples was determined by the Gouy method. When the magnetic properties of the reduced samples were determined, the sealed ampoules containing the reduced samples were opened in a stream of hydrogen. Phase analysis was carried out by means of x-ray patterns, which were obtained with an RKD camera using copper K_α radiation (Ni filter).


SiO2—CrO3 I (Dried in air at 130°)
Treated with air at 515° for 1 hour
T'd with H2 at 515° for 1 hr
Treated with air at 515° for 1 hour
VII Cr2O3—SiO2
Cr2O3—SiO2 II
Cr2O3—SiO2 VIII
Cr2O3—SiO2 IX
Treated with H2 at 515° for 1 hour
Cr2O3—SiO2 III
Treated with air at 515° for 1 hour
Cr2O3—SiO2 IV
Treated with H2 at 515° for 1 hour
Cr2O3—SiO2 VI
Treated with O2 at 515° for 1 hour
Cr2O3—SiO2 V

The original silica gel, after being washed free of Fe and dried, was paramagnetic at 20° with $\chi \cdot 10^6 = -0.29$; after treatment at 515° in a stream of H_2 $\chi \cdot 10^6$ was −0.45. The original preparation of Catalyst 2 − Sample 1 (CrO_3 deposited on silica gel) − was also diamagnetic, $\chi \cdot 10^6 = -0.1$. The susceptibility of all of these samples

TABLE 1

Aromatization of n-Heptane and Cyclohexane at Atmospheric Pressure over $Cr_2O_3 - SiO_2$ Catalysts

Expt. No.	Catalyst No.	Substance	Temp., °C	Space rate, hours^{-1}	Yield based on hydrocarbon fed, wt. %	
					catalyzate	aromatics
1	1A	n-Heptane	535	0,19	65	36
2	1A		535	0,19	74	41
3	1A	Cyclohexane	535	0,14	63	58
4	1A		535	0,17	65	50
5	1A	n-Heptane	510	0,18	71	33
6	1A		510	0,18	66	31
7	1B		535	0,18	61	56
8	1B		535	0,18	65	34
10	1B		535	0,18	70	35
11	2A		510	0,18	66	21
12	2A		510	0,18	70	25
13	2B		510	0,18	64	54
14	2B		510	0,18	73	27
15	2B		510	0,18	72	27

Note. Each succeeding experiment with a given catalyst was carried out after regeneration.

did not depend on field strength over the range studied. Table 2 presents data on the phase composition and magnetic properties of the catalysts studied, I-IX. It may be seen from the data in Table 2 that the samples investigated can be separated into two groups: 1) Paramagnetic catalysts which gave x-ray patterns characteristic

of amorphous materials – Samples II and III*; the temperature dependence of the susceptibility of these catalysts followed the Curie-Weiss law, which permitted calculation of the magnetic moments, 3.2 μB for both samples. 2) Antiferromagnetic Samples IV-IX: these gave x-ray patterns in which all lines were identified as Cr_2O_3 lines.

TABLE 2

Phase Compositions and Magnetic Properties of the Catalysts

Catalyst No.	Catalytic phase	Behavior with respect to Curie-Weiss law	$\chi \cdot 10^6$		
			20°C	80°C	160°C
I	Amorphous	Diamagnetic	—0,10	—0,10	—0,10
II	Amorphous	Obeyed	13,2	11,3	10,1
III	Amorphous	Obeyed	13,2	11,5	10,3
IV	Cr_2O_3	Did not obey	7,5	7,4	7,0
V	Cr_2O_3	Did not obey	7,8	7,6	7,0
VI	Cr_2O_3	Did not obey	8,3	8,1	7,6
VII	Cr_2O_3	Did not obey	7,7	7,6	7,0
VIII	Cr_2O_3	Did not obey	7,3	7,4	6,9
IX	Cr_2O_3	Did not obey	6,7	6,9*	6,5**

*Measured at 60°.

**Measured at 120°.

Thus, Sample VIII, which was prepared from Sample I by heating in a stream of H_2 without preliminary treatment with alcohol, contained crystalline Cr_2O_3, as did Samples V and VI, but Sample III, which was prepared by heating Sample II in a stream of H_2, was paramagnetic and gave an x-ray pattern characteristic of an amorphous material. It may be assumed that in the first case the CrO_3 was reduced directly to Cr_2O_3, while in the second case the treatment with alcohol formed some intermediate chromium compound which was stable in an atmosphere of hydrogen but which formed crystalline Cr_2O_3 when the catalyst was heated in a stream of air. It is possible that this intermediate chromium compound was a chromium silicate, formed during treatment of the catalyst with alcohol, or a nonstoichiometric chromium oxide, which could have formed during the reduction of CrO_3 with alcohol in the absence of mineral acids.

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*The Cr phase in these samples was in a state of very high dispersion. The amorphous x-ray pattern obtained in this case could have been due to scattering by the amorphous carrier, SiO_2, of the weak rays reflected from the very fine crystals.

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NITRATION OF PARAHYDROXYDIPHENYLDIMETHYLMETHANE ACETATE IN THE PRESENCE OF UREA

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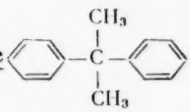
Colbert and Denny [1] have shown that nitration of orthohydroxydiphenyl benzenesulfonate yields the 2'- and 4'-mononitro derivatives. The benzenesulfonate group causes deactivation of all positions in the phenolic ring and is an ortho-para directing substituent with respect to the other ring. The orthobenzoyl group has these same properties [2]. Such selectivity is not observed in the nitration of the acetyl derivative of hydroxybiphenyl, and the nitro group enters both the phenol and the benzene nucleus.

Tsekhanskii [3] has shown that during nitration of symmetrical diphenylalkanes there is a strong activation of the benzene rings with an increase in the length of the carbon chain of the saturated group joined to the benzene ring. In the case of p-hydroxydiphenyldimethylmethane, the presence of both the dimethylmethylene group and the hydroxyl group will promote activation of both rings.

EXPERIMENTAL

Parahydroxydiphenyldimethylmethane  OH. The parahydroxydiphenyldimethylmethane (a crude by-product of the phenol-acetone industry) was purified by recrystallization from a mixture of benzene and petroleum ether. The purified product was obtained in the form of white acicular crystals with an m. p. of 72.5°. According to the literature [4], this compound melts at 73-75°.

Parahydroxydiphenyldimethylmethane acetate. The p-hydroxydiphenyldimethylmethane, 200 g, was added with stirring to 100 g of KOH in 150 g of H_2O. In order to facilitate solution of the phenol in the resulting thick emulsion, 50 ml of ethyl alcohol was added. The acetic anhydride, 180 g, was then rapidly added to the solution. The mixture was cooled during the addition with pieces of ice. The mixture (cooled with ice) was allowed to stand for half an hour, during which time it stratified. The solution was extracted with ether. The ether was distilled leaving a colorless, thick liquid, which distilled at 327° and atmospheric pressure, almost without decomposition. The liquid boiled at 180-182°/1.5 mm. Mol. wt.: found, 250; calculated, 254.

Found %: C 80.35, 80.30; H 7.04, 7.12. Calculated % for $C_{17}H_{18}O_2$: C 80.3; H 7.08.

The amount of product obtained in this experiment was 190 g, which amounted to 80% of theoretical. This acetate had the following constants: d_4^{20} 1.085; n_D^{20} 1.5652; η^{25} 138.1 centistokes; η^{40} 42.4 centistokes; η^{60} 14.5 centistokes. The material was readily soluble in gasoline-range hydrocarbons, benzene, o-xylene, and other solvents.

Nitration of the acetate. Ten grams of this acetate was added, dropwise, and with stirring, to 30 ml of 99% nitric acid containing 7 g of ammonium nitrate. The addition was carried out at 15-20°. Reaction occurred with the evolution of nitrogen oxides. After the nitration mixture had stood for 1 hour at 40° and 1 hour at 60°, it was poured into water containing pieces of ice. A yellow rather viscous mass was formed. Extraction with ether gave a small amount of a solid product, which, after recrystallization from a mixture of ethyl alcohol and carbon tetrachloride, had an m. p. of 122°. A mixture of this material and a known sample of picric acid showed no depression of the melting point. The product dissolved in water with the formation of a yellow solution; when the product was added to a solution of KOH, a yellow crystalline precipitate was formed, which also indicated picric acid.

The formation of picric acid can be avoided if mixing of the acetate and, particularly, the subsequent standing of the reaction mixture are carried out at low temperature. With this procedure, a yellow crystalline compound with a melting point of 127° was formed in low yield. According to the analytical data, this material was the trinitro derivative of p-hydroxydiphenyldimethylmethane. Mol. wt.: found, 356; calculated, 347.

Found %: C 52.88, 52.78; H 4.23, 4.11; N 12.17, 11.93 Calculated % for $C_{15}H_{13}N_3O_7$: C 51.9; H 3.75; N 12.1

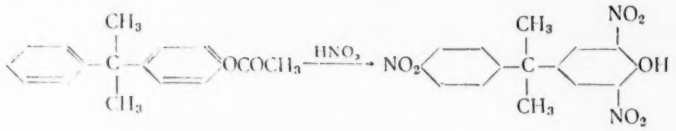
With the aim of avoiding the oxidizing action of the concentrated HNO_3, experiments were carried out on the nitration of the acetate in the presence of urea. Small portions of urea were added to the cooled 99% HNO_3. The p-hydroxydiphenyldimethylmethane acetate was added to this nitric acid, which was free of oxides of nitrogen. The data presented in Table 1 show that the trinitro compound, with an m. p. of 127-127.5°, was formed in appreciably higher yield in the presence of urea. When, however, additon of the urea was carried out after the addition of the acetate to the nitric acid (Experiment 4), only picric acid was formed. This indicates development of oxidation of the phenol acetate, predominately in the initial stage of the nitration.

TABLE 1

Expt. No.	Acetate, g	99% nitric acid, ml	Mole ratio acetate : acid	Ammonium nitrate, g	Urea, g	Addition temp., °C	Standing I		Standing II		Standing III		Product		
							temp., °C	time, hr	temp., °C	time, hrs.	temp., °C	time, hrs.	yield, g	m.p., °C	Mol. wt.
1	5	15	1:18	—	—	10	0—1	2	—	—	—	—	0,9	127	344
2	5	15	1:18	7	—	40	60	0,5	65—70	0,5	—	—	—	121	229
3	5	15	1:18	3,5	3,5	15—17	40	1	60	0,5	80	1	3,8	127,5	—
4*	5	15	1:18	3,5	1	10—15	40	1	60	1	80	0,5	—	122	229
5	5	15	1:18	3,5	1	10	40	1	60	2	—	—	2,9	127	—

*Experiment with the addition of urea after addition of the acetate to the nitric acid.

In order to determine the location of the nitro groups, the nitro compound was subjected to oxidation with chromic acid. A solution was prepared by dissolving 0.42 g of the trinitro compound in 10 ml of concentrated H_2SO_4 in a small beaker. To the solution was added 3.2 g of potassium dichromate in small portions. The contents of the beaker were stirred. During stirring, the temperature rose to 60°, and the solution acquired a green color. The solution was then extracted with ether. The ether extract was dried with calcium chloride, and the ether was distilled; this procedure resulted in a small amount (0.07 g) of a solid, yellow material which was soluble in KOH, yielding a yellow solution. The m. p. was 238-241°. The m. p. of paranitrobenzoic acid is 241°. These data indicate that one of the three nitro groups enters the non-phenolic nucleus of the p-hydroxydiphenyldimethylmethane molecule.



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THE FORMATION OF ORGANOSILICON COMPOUNDS DURING THE INTERACTION OF SILICON HYDRIDES AND OLEFINS IN THE PRESENCE OF IRON PENTACARBONYL

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We have previously shown [1] that the interaction of triethylsilane with vinyl ethyl ether in the presence of $Fe(CO)_5$ yields an unsaturated compound having the structure $(C_2H_5)_3SiCH = CHOC_2H_5$.* In contrast, the reaction of silanes with olefins in the presence of iron pentacarbonyl led to the formation of unsaturated addition products [1]. A more detailed study of this problem showed that, in a number of cases, the reaction between silicon hydrides and olefins in the presence of iron pentacarbonyl can take place by two routes, 1 and 2 below:

$$HSiR'R''R''' + CH_2=CHR \xrightarrow{Fe(CO)_5} \begin{cases} \longrightarrow R'R''R'''SiCH_2CH_2R & (1) \\ \longrightarrow R'R''R'''SiCH=CHR & (2) \end{cases}$$

It was found that an excess of the silane favored reaction in accordance with Scheme 1, while an excess of the olefin favored reaction by Scheme 2. Another important factor affecting the direction of the reaction is the structure of the silicon hydride; the use of methyldichlorosilane promoted the formation of saturated reaction products, while the use of triethylsilane favored the formation of unsaturated products.

Thus, tetraethylsilane and a small amount of symmetrical hexaethyldisilylethane were formed during the interaction of triethylsilane with ethylene at a mole ratio of silane to ethylene of 3:1 in the presence of iron pentacarbonyl. When the reaction was carried out at a mole ratio of triethylsilane to ethylene of 1:5, triethylvinylsilane was obtained.

We also studied the reaction of methyldichlorosilane with ethylene, propylene, and 1-decene. The reaction was carried out both in the presence of excess silane and of excess olefin. As we have reported previously [1], only the addition product – methylethyldichlorosilane – was formed in the case of the reaction with ethylene. No vinylmethyldichlorosilane was found in the reaction mixture when the mole ratio $CH_3SiCl_2H/CH_2=CH_2$ was varied from 1:4 to 1:7. A mixture of saturated and unsaturated products was formed in the other two cases, and in the case of the reaction between methyldichlorosilane and decene, the composition of the reaction mixture of unsaturated ($CH_3SiCl_2C_{10}H_{19}$) and saturated ($CH_3SiCl_2C_{10}H_{21}$) products varied only slightly with a change in the ratio of initial silane to decene from 1:2 to 5:1.

In the case of the reaction of methyldichlorosilane with propylene at a mole ratio of 3:1, the resulting mixture of $CH_3SiCl_2C_3H_7$ (I) and $CH_3SiCl_2C_3H_5$ (II) contained 75% (I) and 25% (II). At a mole ratio of reactants of 1:4, the mixture contained 24% (I) and 76% (II).

* The structure of this compound was confirmed in the present work through a study of the i. r. spectrum, thiocyanation, and hydrolysis.

In a study of the reaction of methyldichlorosilane with 1-decene it was shown that the reaction with olefins is catalyzed only by iron pentacarbonyl without the participation of any co-catalyst; this is in contrast to the reaction with acrylonitrile, which we have described previously [2]. As a matter of fact, methyldichlorosilane and 1-decene react in the presence of iron pentacarbonyl either in sealed glass ampoules or in an autoclave with the formation of the same products in the same yields. In a continuation of the study of this same reaction, it was established that, when the reaction proceeds in accordance with Scheme 2, the hydrogen acceptor is the decene, which is thereby hydrogenated to n-decane.

It may be assumed that the reaction proceeds through the formation of a radical or a cation of the structure $CH_3SiCl_2CH_2\overset{\circ}{C}HCH_2C_7H_{15}$ (A) (where the $\overset{\circ}{C}$ denotes a positive charge or an unpaired electron). Fragment A is hydrogenated during reaction with the silane, and is dehydrogenated during reaction with the olefin. The reaction can be represented in a somewhat simplified manner by the scheme:

$$R'R''R'''Si\overset{\circ}{C}H + CH_2{=}CHR \rightarrow R'R'R'''SiCH_2\overset{\circ}{C}HR \quad \text{(A)}$$

$$A \xrightarrow{HSiR'R''R'''} R'R''R'''SiCH_2CH_2R + R'R''R'''\overset{\circ}{S}i$$

$$A \xrightarrow{CH_2=CHR} R'R''R'''SiCH(CHR)_2 + CH_3\overset{\circ}{C}HR$$

$$CH_3\overset{\circ}{C}HR + HSiR'R''R''' \rightarrow CH_3CH_2R + \overset{\circ}{S}iR'R''R'''$$

EXPERIMENTAL

Reaction of triethylsilane with ethylene. With excess ethylene. (Preparation of triethylvinylsilane). To a half-liter, stainless steel autoclave were charged 34 g $(C_2H_5)_3SiH$ and 0.5 ml of $Fe(CO)_5$. The air was purged from the autoclave with nitrogen, and ethylene was then introduced to a pressure of 45 atm. The reaction mixture was heated to 130° for five hours, during which time the pressure dropped from 70 to 35 atm. From the 39.5 g of product was separated 27 g (66% of theoretical) of triethylvinylsilane. After a second distillation, this product boiled at 144.5°; n_D^{20} 1.4330; d_4^{20} 0.7718. MR: found, 47.92; calculated* for $C_8H_{18}Si$, 48.26. Literature values of these properties are given in reference [4].

Found %: C 67.27, 67.39; H 12.96, 13.18. Calculated % for $C_8H_{18}Si$: C 67.57; H 12.75.

The Raman spectrum** of the material agreed with that reported for triethylvinylsilane [5]. This product was completely soluble in concentrated sulfuric acid, and dilution of the acid yielded only hexaethyldisiloxane (b. p., 233°; n_D^{20} 1.4328; d_4^{20} 0.8448). MR: found, 75.85; calculated for $C_{12}H_{30}Si_2O$, 76.08. Literature values for these properties are given in reference [6].

In a repitition of this experiment but with an initial ethylene pressure of 5 atm. (the pressure dropped from 20 to 10 atm. during the reaction, which was carried out at 130°), $(C_2H_5)_4Si$ was obtained in a yield of 73% of theoretical, calculated on the basis of the triethylsilane reacted***; hexaethyldisilylethane was also obtained in a yield of 20%.

Reaction of methyldichlorosilane with 1-decene. The reaction was carried out in the manner described above. A mixture of 63 g (0.45 mole) of decene, 70 g (0.6 mole) of CH_3SiCl_2H, and 0.2 ml of $Fe(CO)_5$ was heated in a steel autoclave at 140° for five hours****. Distillation of the reaction products gave the following fractions: 1) 40-60°, 34 g (unreacted CH_3SiCl_2H); 2) 169-175°, 35 g; 3) 122° at 3 mm, 52 g.

Fraction 2, which was a mixture of decene and decane, was treated with sulfuric acid. The insoluble organic layer was separated and washed. There was obtained 24.1 g of a fraction with a b. p. of 74° at 30 mm; n_D^{20} 1.4121; d_4^{20} 0.7325. MR: found, 48.52.; calculated for $C_{10}H_{22}$, 48.53.

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*The molar refraction calculations reported in the present paper were calculated using the group contributions proposed by V. F. Mironov and G. I. Nikishin [3].

**All of the spectra cited in the present paper were taken and interpreted by L. A. Leites, for which the authors express their sincere appreciation.

***For the sake of accuracy, it should be mentioned that the yields reported in our previous article [1] for the reaction of ethylene with triethylsilane referred to the mixture of all organosilicon compounds obtained in the experiments.

****Similar results were obtained when the reaction was carried out in sealed glass ampoules.

Found %: C 84.15, 84.15; H 15.56, 15.45. Calculated % for $C_{10}H_{22}$: C 84.22; H 15.58.

The i. r. spectrum and physical constants were in agreement with the data reported in the literature.

Fraction 3, which was a mixture of $CH_3SiCl_2C_{10}H_{21}$ (I) and $CH_3SiCl_2C_{10}H_{19}$ (II), was redistilled; n_D^{20} 1.4571; d_4^{20} 0.9742.

Found %: C 52.06, 51.96; H 8.68, 8.87; Cl 27.34, 27.86; Si 11.24, 11.11. Calculated % for $C_{11}H_{24}SiCl_2$: C 51.76; H 9.41; Cl 27.83; Si 11.00. Calculated % for $C_{11}H_{22}SiCl_2$: C 52.28; H 8.75; Cl 28.00; Si 11.08.

The mixture was methylated by Grignard reaction. This gave a fraction boiling at 85-86°/1 mm (75% yield); n_D^{20} 1.4390; d_4^{20} 0.7797.

Found %: C 73.36, 73.62; H 13.42, 13.43; Si 13.00, 12.89. Calculated % for $C_{13}H_{28}Si$: C 73.50; H 13.18; Si 13.21. Calculated % for $C_{13}H_{30}Si$: C 72.81; H 14.10; Si 13.09.

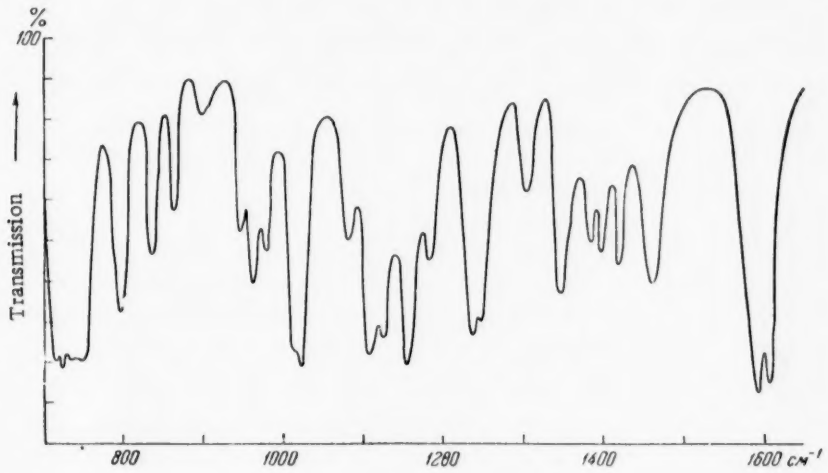

Fig. 1.

The resulting trimethyl derivative gave a Raman spectrum in the region of the C=C frequency which had two lines: one at 1615 cm^{-1} and a split band at 1662-1670 cm^{-1}. It may apparently be concluded that this substance was a mixture of $Me_3SiCH = CH - C_8H_{17}$ (III) and $Me_3SiCH_2CH = CHC_7H_{15}$ (IV). Proof of the presence of (III) was the line at 1615 cm^{-1} (1620 cm^{-1} has been reported for a compound of this type [7]). Proof of the presence of (IV) was splitting of the band at 1662-1670 cm^{-1} and the presence in the spectrum of a line at 1155 cm^{-1}, which is characteristic of compounds containing a double bond in the position beta to a silicon [8]. Splitting of the band at 1662-1670 cm^{-1} is probably due to the presence of cis and trans isomers [8, 9].

On the basis of the yields obtained, the n-decane content of the unsaturated compounds in the mixture comprised 73%, calculated on the basis of the equation $CH_3SiCl_2H + 2C_{10}H_{20} \rightarrow CH_3SiCl_2C_{10}H_{19} + C_{10}H_{22}$.

Treatment of this mixture with concentrated sulfuric acid showed that this substance consisted of a saturated, sulfuric acid-insoluble product (~40%) and an unsaturated sulfuric acid-soluble compound (~60%). When the sulfuric acid layer was diluted with water, only hexamethyldisiloxane separated, b. p. 97-99°, n_D^{20} 1.3750; d_4^{20} 0.7676. MR: found, 48.43; calculated for $C_6H_{18}Si_2O$, 49.02. Literature values for these properties are given in reference [6]. It should be mentioned that partial decomposition of the saturated silane occurred upon treatment of the mixture of $CH_3SiCl_2C_{10}H_{21}$ and $CH_3SiCl_2C_{10}H_{19}$ with sulfuric acid, since n-decane was isolated during fractionation of the sulfuric acid-insoluble layer.

Reaction of methyldichlorosilane with propylene. From 60 g (0.52 mole) of $CH_3SiC_{12}H$, 84 g (2 mole) of C_3H_6, and 1 ml of $Fe(CO)_5$ was obtained 40 g of a fraction with a b. p. of 124-130°, n_D^{20} 1.4380; d_4^{20} 1.0553.

Found %: C 30.99, 30.97; H 5.58, 5.58; Si 17.91, 17.63; Cl 45.45, 45.44. Calculated % for $C_5H_8SiCl_2$: C 30.98; H 5.19; Si 17.09; Cl 45.83. Calculated % for $C_4H_{10}SiCl_2$: C 30.59; H 6.42; Si 17.85; Cl 45.15.

Methylation with Grignard reagent and subsequent treatment gave a fraction with a b. p. of 87-88°, n_D^{20} 1.4042; d_4^{20} 0.7147.

Found %: C 62.68, 62.83; H 12.92, 12.86. Calculated % for $C_6H_{14}Si$: C 63.08; H 12.35. Calculated % for $C_6H_{16}Si$: C 61.98; H 13.87.

The Raman spectrum of the trimethyl derivative showed lines belonging to $(CH_3)_3SiCH = CHCH_3$ [7] and $(CH_3)_3SiCH_2CH_2CH_3$ [10].

Treatment with sulfuric acid showed that the mixture contained 25% of the saturated silane with a b. p., of 87-88°, n_D^{20} 1.3950; d_4^{20} 0.7050. MR: found, 39.53; calculated for $C_6H_{16}Si$, 39.49.

Found %: C 62.53, 62.59; H 14.02, 14.20. Calculated % for $C_6H_{16}Si$: C 61.98; H 13.87.

Literature values for these properties are given in references [11].

The infrared spectrum was in agreement with that of a known sample of $(CH_3)_3SiCH_2CH_2CH_3$.

When the sulfuric acid layer was diluted with water, only hexamethyldisiloxane was obtained.

The results obtained upon thiocyanation of this mixture also confirmed the presence of unsaturated compounds. Thiocyanometric bromine number: found, 63.5 after 1 hour, 98 after a day; calculated for $(CH_3)_3SiCH_3H_5$, 140.3. The content of unsaturated compounds in the mixture was 70%.

Investigation of the structure of $(C_2H_5)_3SiCH = CHOC_2H_5$ (V). The thiocyanometric iodine number found for (V) was 85.7 after 5 minutes, 97.4 after 0.5 hour, and 109.5 after 1 hour. The calculated value is 85.9. The increase observed in the thiocyanometric bromine number was apparently due to side reactions. Acid hydrolysis of (V) was carried out by treatment with a sulfuric acid solution of 2,4-dinitrophenylhydrazine. Acetaldehyde hydrazone was obtained; m. p. 146° (from alcohol).

Found %: N 25.09 and 25.19; calculated % for $C_8H_8N_4O_4$: 24.99.

The infrared spectrum of (V) was taken with an IKS-14 apparatus (Fig. 1). Splitting of the double bond band into two components at 1597 and 1609 cm^{-1} is characteristic of vinyl ethers, and has been observed previously [12-14]. The authors of these references explained this phenomenon by rotation isomerism.

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NEW METHODS FOR THE PREPARATION OF HEXAFLUOROPLATINATES:

FLUORINATION WITH CHLORINE TRIFLUORIDE

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In a previous communication [1], we presented a review of methods of synthesis of complex fluorides of tetravalent platinum and described the work of other authors on the synthesis of potassium hexafluoroplatinate starting with bromine pentafluoride and metallic platinum. The fluorination mechanism was established; it is based on the formation of bromine monofluoride and difluorobromonium hexafluoroplatinate. The present work was undertaken with the aim of developing a more convenient method for the preparation of potassium hexafluoroplatinate.

It is well known that chlorine trifluroide is the most active fluorinating agent of all of the fluorine compounds. Moreover, it has still another advantage in that the fluorination results in the formation of only potassium hexafluoroplatinate, unaccompanied by any by-products, and this obviates the necessity of the lengthy operations of heating under vacuum to separate halogen fluoride.

In consideration of this fact, we studied the action of chlorine trifluoride on a mixture of platinum and potassium bifluoride and also on potassium hexachloroplatinate. It was found that when a platinum boat containing a mixture of 5 g of platinum black and 3 g of potassium bifluoride is heated at 200° in a stream of chlorine trifluoride, the platinum is completely converted to potassium hexafluoroplatinate, which may then be separated from the excess potassium bifluoride by recrystallization from hot water.

Still better results were obtained by converting potassium hexachloroplatinate to potassium hexafluoroplatinate through the agency of chlorine trifluoride. Our experiments showed that liquid ClF_3 has almost no effect on K_2PtCl_6 – only an insignificantly small amount of the light-colored phase was formed after this salt had stood in liquid chlorine trifluoride at 0° for 24 hours; however, the reaction with gaseous ClF_3 proceeded rapidly at 500° and led to complete replacement of the chlorine by fluorine. The experiments were carried out in a quartz tube, in which was placed a nickel boat containing potassium hexachloroplatinate (15 g). As conversion proceeded, the product color became lighter and chlorine was evolved. Toward the end of the reaction, the salt became a light yellow, and the loss in weight corresponded precisely to that calculated in accordance with the equation:

$$K_2PtCl_6 + 2ClF_3 = K_2PtF_6 + 4Cl_2. \quad (1)$$

It was then necessary to confirm that the resulting product contained no chlorine.

Under the conditions described, the process is complete in approximately $1^1/_2$ hours. Inasmuch as K_2PtF_6 interacts at high temperature with atmospheric moisture, it was necessary to wait until the boat had cooled before removing it from the quartz tube. The purity of the potassium hexafluoroplatinate obtained by this method depended only on the purity of the original K_2PtCl_6. If necessary, the preparation can be purified by recrystallization from water. Crystals obtained in this way were identical to those previously obtained. The

composition of the salt was confirmed both by correspondence of the weight loss with that calculated from Equation (I) and by analysis. We had previously developed a method for analyzing potassium hexafluoroplatinate based on pyrohydrolysis of a weighed sample with superheated steam; the method has been reported earlier [1]. However, this method requires considerable expenditure of time; therefore, we have developed still another method of analysis, which is sufficiently accurate and can be carried out rapidly.

A weighed sample of the salt, 0.2 to 0.4 g, was mixed with calcined soda (1 g) in a platinum boat. The surface of the mixture was covered with a layer of soda. The boat was placed in a quartz tube and heated in a stream of hydrogen for 15-20 minutes at 400°.

The boat was cooled and weighed to determine the loss in weight, which corresponded to that calculated from the equation:

$$K_2PtF_6 + H_2 + 2Na_2CO_3 = 2KF + 4NaF + Pt + 2H_2O + 2CO_2.$$

The sample was then transferred to a filter and leached with hot water; the platinum remaining on the filter was calcined and weighed. The fluorine in the filtrate was determined as PbClF, and the potassium was determined as K_2PtCl_6. The entire analysis can be carried out in one day.

The results obtained in the analysis of the potassium hexafluoroplatinate are:

K_2PtF_6	Found %	Pt 50,7 ± 0,2;	F 29,5 ± 0,3;	K 20,0
	Calculated %:	Pt 50,37;	F 29,43;	K 20,13

The density of this preparation was 4.79 g/cc, as determined pycnometrically. According to the literature, the density is 4.83 g/cc.

The results of experiments carried out under the same conditions but using gaseous fluorine as the fluorinating agent showed that this reagent also converts K_2PtCl_6 to the hexafluoroplatinate; however, the product yield was significantly lower, and, consequently, this preparation required purification by recrystallization.

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THE EFFECT OF THE NATURE OF METALS ON THEIR CATALYTIC ACTIVITY

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According to the multiplet theory of A. A. Balandin [1], an essential condition for catalysis is a structural and energy correlation between the reacting chemical bonds in the substratum and catalyst. The correlation [2] gives rise to the principle of the preservation of the valence angle, which has been discussed by many authors (see, for example, [3]). This principle requires the existence of a regular relation between catalytic activity and, consequently, the activation energy, and the interatomic distances in the case of catalysts with similar structures. The existence of such a relation has been confirmed in a number of cases (Eckel [4], Rubinshtein [5], and Beeck [6]). On the other hand, the electronic theories of catalysis (which are being developed in the USSR mainly by S. Z. Roginskii [7] and F. F. Vol'kenstein [8]) require a relation between catalytic activity and the electronic properties of a solid catalyst. For this reason some investigators compare the catalytic activity of a metal with the work function [9], with the incompleteness of filling of the d-level [10,11], with the d-character of the metallic bond [12, 13], and also with magnetic properties [14].

TABLE 1

Comparison of Activation Energies for Dehydrogenation of Isopropyl Alcohol with Physical Properties of the Metallic Catalysts Investigated

	Fe	Co	Ni	Cu	Pd	Ag	Pt
Atomic number	26	27	28	29	46	47	78
ϵ, kcal/mole	20,0	12,4	8,9	10,7	18,0	19,5	17,2
Crystal structure	A2	A3	A1	A1	A1	A1	A1
Interatomic distance [17], Å	2,48	2,51	2,49	2,56	2,75	2,89	2,77
Work function [18], v	4,36	4,18	4,86	4,47	4,82	4,28	5,29
Content of electronic d-vacancies	2,2	1,7	0,6	0,0	0,60	0,0	0,55
d-Character of the metallic bond, %	39,7	39,5	40,0	36,0		36,0	44,0
Heat of atomization, kcal/mole	99	102	101	81	110	65	122

The authors of the present work thoroughly studied the dehydrogenation of alcohols over various metallic catalysts [15, 16]. From the point of view of the theory of catalysis, it was interesting to compare the activation energies obtained with the values characterizing various properties of the metals, used as catalysts. Such a comparison is given in Table 1 for the dehydrogenation of isopropyl alcohol. As a special investigation showed, in the case of a copper catalyst [15] the kinetic constants characterizing dehydrogenation of various alcohols depended little on the alcohol structure. This is apparently due to the similar orientation of alcohols. Consequently, with a high degree of probability, we can extend the results of investigating the kinetics of isopropyl

alcohol dehydrogenation to other alcohols, so that the results in Table 1 have a quite general character.

Examination of Table 1 shows that there is a parallelism between activation energies and interatomic distances in the case of metals with a most densely packed crystal lattice (face-centered A1 or hexagonal A3). As Fig. 1 shows, over the range investigated the activation energy for alcohol dehydrogenation ϵ increased with an increase in the distance between the metal atoms d. This increase was linear, in contrast to the relation of activity (not ϵ) to d in [4-6], where a maximum was observed. The existence of a regular relation between activation energy and interatomic distance agrees with the multiplet theory. On the other hand, an examination of Table 1 shows that the electronic properties taken separately (including work function and percent of d-character), as well as the heat of atomization, cannot explain the course of the changes in the activation energy values. No direct parallelism was observed in this case between the separate electronic properties and the activation energy. However, this does not contradict the essence of the electronic theory of catalysis. Obviously, structural and energy factors are based on the fact that matter is constructed from electrons and nuclei. However, quite a complicated combination of electronic properties is required apparently to explain catalysis, while such a combination often exists already in structural (and energy) factors.

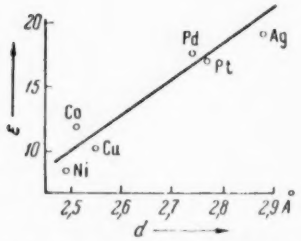

Fig. 1. Relation of activation energy of isopropyl alcohol dehydrogenation to the shortest interatomic distance in the metal crystal lattice (A1 and A3 lattices).

In the present work we studied experimentally the dehydrogenation of isopropyl alcohol on metallic silver, platinum and palladium. Platinum and palladium were prepared by reducing chloroplatinic and chloropalladic acids with formalin by N. D. Zelinskii's method. The silver catalyst was prepared by hydrogen reduction of silver oxide, obtained by precipitation from an aqueous solution of $AgNO_3$. The procedure for the kinetic measurements was described previously [10, 11]. The rate constant of the reaction k was calculated by the formula

$$k = (z_2 + z_3) A_1 \ln \frac{A_1}{A_1 - m} - (z_2 + z_3 - 1) m, \quad (1)$$

obtained from the general kinetic equation derived by one of the authors [19] (here A_1 is the space velocity of the alcohol, m is the volume of hydrogen evolved per min in 1 ml at s. t. p., and z_2 and z_3 are the relative

TABLE 2

Relative Adsorption Coefficients of Acetone (z_2)

Catalyst	Temp. °C	$z_2 = a_{ac}/a_{alc}$
Ag	250	1,00±0,03
Ag	267	0,98±0,05
Ag	289	0,96±0,05
Pt	235	0,30±0,03
Pt	248	0,32±0,03
Pt	268	0,30±0,06

TABLE 3

Relative Adsorption Coefficients of Hydrogen (z_3)

Catalyst	Temp., °C	$z_3 = a_{H_2}/a_{alc}$
Ag	257	0,47±0,09
Ag	272	0,44±0,05
Ag	287	0,47±0,04
Pt	226	0,32±0,04
Pt	244	0,42±0,04
Pt	256	0,45±0,05
Pt	272	0,54±0,08
Pt	282	0,60±0,01

adsorption coefficients of acetone and hydrogen). As Formula (1) shows, the calculation of the reaction rate constants required the determination of z_2 and z_3 of the reaction products. The values of z_2 and z_3 were determined by a reaction-kinetic method [20]. The procedures for the determination and calculation are described in [15 and 16]. The data obtained are given in Tables 2 and 3.

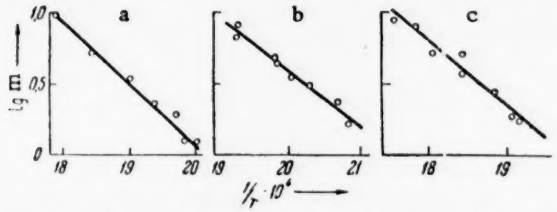

Fig. 2. Relation of log m to 1/T for isopropyl alcohol dehydrogenation: a) Over Ag; b) over Pt; c) over Pd.

In order to determine the activation energy of isopropyl alcohol dehydrogenation, we carried out a series of experiments at different temperatures but a constant space velocity. To calculate the value k, the values of A, m, and $(z_2 + z_3)$ were substituted in Formula (1). For a platinum catalyst z_3 increases with an increase in

TABLE 4

Dehydrogenation of iso-C_3H_7OH over Ag (catalyst volume 10 ml); flow rate 0.16 ml/min; A_1 = 47.4 ml/min; A_1' = 4.74 ml/min per ml of catalyst; $z_2 + z_3$ = = 1.44; ϵ = 19500 cal/mole; $k_0 = 2.31 \cdot 10^8$, $\epsilon / \lg k_0 = 2.27 \cdot 10^3$)

Expt. No.	Temp. °C	m_{H_2}, ml/min	m_{H_2}', ml/min per ml cat.	k	k_{cal}
1	228	1,14	0,114	0,123	0,119
7	232	1,22	0,122	0,125	0,140
3	236	1,85	0,185	0,190	0,164
6	244	2,08	0,208	0,223	0,226
2	254	3,30	0,330	0,341	0,327
4	270	4,93	0,493	0,536	0,555
5	287	8,80	0,880	1,010	0,920

TABLE 5

Dehydrogenation of iso-C_3H_7OH over Pt (volume of catalyst 1 ml; flow rate 0.16 ml/min; A_1 = 47.4 ml/min, A_1' = 47.4 ml/min per ml of catalyst; ϵ = 17200 cal/mole; $k_0 = 7.36 \cdot 10^7$, $\epsilon / \log k_0 = 2.12 \cdot 10^3$)

Expt. No.	Temp. °C	m_{H_2}', ml/min per ml cat.	z_2+z_3	k	k_{cal}
1	206	1,62	0,56	1,63	1,75
6	210	2,12	0,58	2,16	2,08
7	219	2,76	0,61	2,88	2,86
5	225	3,20	0,64	3,26	3,52
4	230	3,90	0,66	4,07	4,24
3	231	4,23	0,66	4,39	4,24
2	245	6,92	0,72	7,28	6,56
8	245	5,85	0,72	6,12	6,56

temperature (see Table 3) and so the value of z_3 for the required temperature was found by interpolation from the graph of the relation of lg z_3 to 1/T. We determined the true activation energy for the dehydrogenation of isopropyl alcohol over silver and platinum, as the relative adsorption coefficients of the reaction products had been determined for these catalysts. An approximate activation energy was calculated for palladium from the

TABLE 6

Dehydrogenation of iso-C_3H_7OH over Pd (volume of catalyst 1 ml, flow rate 0.15 ml/min; A_1 = 45.0 ml/min; A_1' = 45.0 ml/min per ml of catalyst; ϵ = 18000 cal/mole)

Expt. No.	Temp., °C	m_{H_2}, ml/min per ml of cat.	Expt. No.	Temp., °C	m_{H_2}, ml/min per ml of cat.
7	249	1,77	8	268	3,33
1	250	1,82	3	280	4,71
2	257	2,53	4	288	6,56
6	268	4,20	5	296	7,70

the slope of the line of the relation of lg m to 1/T. See Tables 4-6 and Fig. 2 for the values obtained for ϵ. As Fig. 2 shows, the points fall on Arrhenius lines with sufficient accuracy. The activation energies found and the activation energies from papers [15 and 16] are in Table 1.

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OPTICAL INVESTIGATION OF GEOMETRIC AND ROTATIONAL ISOMERISM OF SOME DIENES

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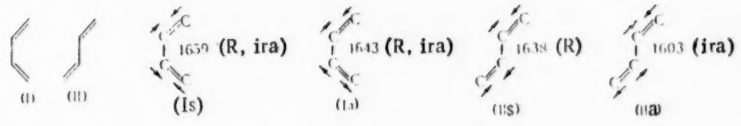
1,3-Butadiene exists in the form of two planar conformations, namely, cisoid (I) and transoid (II) [1]. In these conformations the vibrations of the double bonds are not independent, but are connected by one single C–C bond, which causes two forms of these vibrations, namely, symmetrical (s) and antisymmetrical (a). The frequencies of all these vibrations are different. The transoid conformation (II) has a center of symmetry and consequently its Raman spectrum (R) should contain only one higher frequency of the symmetrical vibration (1638 cm^{-1}) while, on the other hand, the infrared absorption spectra (i. r. a.) should show only one lower frequency of the antisymmetrical vibration (1603 cm^{-1}), which was actually found experimentally for the spectra of 1,3-butadiene, plotted at room temperature [2-4]:

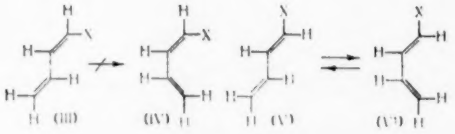


The data presented indicate that in 1,3-butadiene at room temperature there is an absolute predominance of the transoid planar conformation (II) (according to a combination of physicochemical data, up to 96%). The cisoid conformation of 1,3-butadiene (I) has no center of symmetry and, consequently, the Raman and infrared absorption spectra of this conformation should contain both forms of vibration of the double bonds (Is) and (Ia) with frequency (Ia) more intense in the former and frequency (Is), in the latter. In the Raman spectrum [4] they are actually observed for 1,3-butadiene in the gas phase at 55° at 1643 and 1659 cm^{-1} and the former is much more intense than the latter; they both lie at higher wavelengths than with (II) due to the higher energy stress of (I)*. In the infrared absorption spectrum, that frequency at ~1659 cm^{-1} should be more intense; it has been observed [3] at room temperature as a weak band. Under these conditions the cisoid form of 1,3-butadiene is present only as a trace in the transoid form; the frequency of ~1643 cm^{-1} would be extremely weak under these conditions and naturally it was not detected.

What has been stated is confirmed chemically: At room temperature 1,3-butadiene undergoes the Diels–Alder reaction only slowly due to the absolute predominance of the transoid conformation (II) under these conditions. This reaction is accomplished more readily at an elevated temperature, which promotes the conversion of the transoid (II) into the cisoid conformation (I), that is precisely the basis of the Diels–Alder reaction.

* The considerably higher double bond vibration frequencies for the cisoid conformation (I) of 1,3-butadiene than for ethylene (1621 cm^{-1}) indicates considerable shortening of the double bonds in (I) in comparison with the double bond in ethylene [2].

In the mono- and disubstituted 1,3-butadienes below that we investigated rotational isomerism is possible as in 1,3-butadiene, but in some cases it is superposed on geometrical isomerism as, for example, in 1-chloro-1,3-butadiene and piperylene (1,3-pentadiene).* Due to this superposition, for the latter compounds we can propose the following four possible isomers (X = Cl, CH_3):



Naturally, as in the case of 1,3-butadiene itself, in these substituted 1,3-butadienes the transoid conformation (III) and (V) predominate at room temperature in the liquid phase. They have no center of symmetry and therefore their Raman (like the infrared absorption) spectra should contain the frequencies of both forms of double bond vibrations, i.e., symmetrical and antisymmetrical, and for (V) (like the trans configuration of a disubstituted ethylene) these frequencies must be higher than for (III) (like the cis configuration of a disubstituted ethylene).

TABLE 1

cis (III)	Mix. of cis + trans		cis (III)	Mix. of cis + trans		cis (III)	Mix. of cis + trans	
	trans (V)	cis (III)		trans (V)	cis (III)		trans (V)	cis (III)
Raman spectrum of cis-1-chloro-1,3-butadiene and a mixture of cis- and trans-1-chloro-1,3-butadienes of transoid conformation								
175 (5*)	—	174 (4*)	—	912 (4*)	—	1640 (10**)	—	1640 (3**)
184 (4*)	—	185 (3*)	929 (6ш)	—	929 (5*ш)	—	1649 (3**)	—
366 (8*)	—	366 (6)	—	1157 (6)	—	—	1669 (3**)	—
—	398 (3ш, дв)	—	1226 (10ш)	—	1226 (8ш)	2846 (1)	—	2846 (0)
—	466 (5)	—	1279 (5*)	1282 (6*)	Coincide	2917 (1)	—	2919 (0)
628 (3*)	—	628 (2*)	1291 (5*)	—	1293 (3*)	—	2945 (0)	—
643 (3*)	—	642 (2*)	1302 (5*)	—	1304 (3*)	2954 (3*)	—	2956 (1*)
—	663 (1)	—	1325 (4р)	—	1325 (2р)	2973 (3*)	—	2972 (1*)
—	745 (3*)	—	1360 (ош, дв)	—	1360 (ош, дв)	—	3000 (3*)	—
752 (5)	—	754 (4*)	—	1408 (2*)	—	3014 (10)	—	3014 (7*)
—	810 (4)	—	1421 (6)	—	1421 (4*)	3091 (6)	—	3090 (4**)
—	839 (4)	—	1625 (10**)	—	1625 (9**)	—	3101 (2**)	—
Raman spectrum of cis-piperylene and a mixture of cis- and trans-piperylenes of transoid conformation								
—	191 (2)	—	—	1015 (0)	—	—	1434 (0)	—
206 (2*)	208 (2)	—	1035 (3ш)	1035 (3дв)	—	1439 (5**)	—	—
214 (2*)	—	—	—	1080 (3дв)	—	1454 (5**)	1452 (6*)	—
228 (2)	—	—	—	1110 (3*)	—	—	1462 (4*)	—
363 (4дв)	—	—	—	1127 (3*)	—	1638 (10*)	—	1637 (2**)
392 (8)	—	390 (3)	1166 (6)	—	1165 (2**)	—	1645 (10**)	—
—	458 (1)	—	—	1175 (8**)	—	1656 (10*)	—	1656 (2**)
—	481 (8р)	—	—	1190 (8**)	—	—	1670 (7**)	—
615 (1*)	—	613 (0)	1252 (9ш)	—	1253 (4ш)	—	2854 (4*)	—
626 (2*)	—	—	—	1292 (9ш*)	—	2857 (3**)	—	—
—	815 (4ш)	—	1297 (8ш)	—	1297 (3*)	—	2885 (4*)	—
886 (4**)	—	—	1325 (0)	—	—	2918 (6**)	2917 (8*)	—
—	889 (5*)	—	—	1352 (0)	—	2961 (0**)	—	—
902 (4**)	902 (5)	—	1361 (2)	—	—	—	2968 (2*)	—
914 (2**)	—	—	—	1378 (5)	—	2991 (2**)	—	—
—	952 (0**)	—	1387 (4*)	—	—	—	2996 (9*)	—
958 (5)	—	—	1397 (0*)	—	—	3014 (8**)	3012 (4*)	—
—	965 (0**)	—	—	1416 (5)	—	3085 (3)	3089 (5)	—

Footnote: The stars denote lines lying on a background common to neighboring lines, denoted by the same number of stars. ш = broad, дв = double, р = sharp.

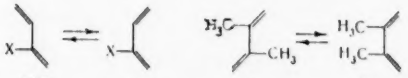
We actually observed all this. We investigated the Raman spectra of (III) [cis-1-chloro-1,3-butadiene (see [8] for the synthesis) and cis-piperylene]. The spectra contained the frequencies of both forms of double bond

*Available literature data on the Raman spectra of some of the compounds we investigated are very unsatisfactory; some of them [5, 6] have gross errors and other spectra were obtained almost 30 years ago [7] on instruments of low resolving power with substantial omissions and hence inaccuracies in the region of double bond vibration frequencies, which is important for our investigation.

vibrations, i.e., symmetrical and antisymmetrical: with X = Cl, 1625 and 1640 cm^{-1} and X = CH_3, 1638 and 1656 cm^{-1}. We then investigated the Raman spectra of trans-1-chlorobutadiene, and trans-piperylene, which were not obtained in a pure form, but as mixtures with forms of cis configuration [8]. The spectra of the trans forms also contained frequencies of both symmetrical and antisymmetrical vibrations of double bonds: with X = Cl, 1649 and 1669 cm^{-1} and with X = CH_3, 1645 and 1670 cm^{-1}. As the optical investigation showed, there was ~20% of the trans form in the mixture of cis- and trans-1-chloro-1,3-butadienes and~80% of the trans form in the mixture of cis- and trans-piperylenes (see Table 1*). In accordance with what has been said above, the frequencies of the double bond vibrations of the trans form of both compounds were higher than those of the cis forms.

Chemical data were in agreement with what has been stated above: with the cis configurations of the transoid conformation (III) where X = Cl or CH_3 there was no Diels-Alder reaction even at an elevated temperature,as in this case (III) could only change into the cis configuration of the cisoid conformation (IV), which could not be realized or was difficult to realize due to steric hindrance. On the other hand, with the trans configurations of the transoid conformation (V) there was a Diels–Alder reaction at an elevated temperature as under these conditions they changed into the trans configuration of the planar cisoid conformation (VI), which promoted this reaction.

For chloroprene and isoprene one may propose two possible planar conformations, namely, a transoid (VII) and a cisoid (VIII) (X = Cl or CH_3), and (IX) and (X) for 2,3-dimethylbutadiene and of these, (VII) and (IX) will predominate at room temperature.



(VII) (VIII) (IX) (X)

As conformation (VII) has no center of symmetry, in the Raman spectrum (and also the infrared absorption spectrum) it should be characterized by both forms of double bond vibrations, i.e., symmetrical and antisymmetrical, like the cisoid conformations (VIII) and (X). Due to the presence of a center of symmetry in it, the

TABLE 2

Raman Spectra of Chloroprene, Isoprene, and 2,3-Dimethylbutadiene

Chloroprene, $\Delta\nu$ cm^{-1}: 236(1*), 247(3*), 259(1*), 378(1**), 388(4**), 397(1*), 511(0*), 518(5*), 535(1*), 631 (7), 881 (3*) 891 (1*), 919 (3**), 931 (3**), 1010(1*), 1021 (4*), 1032 (1*), 1217 (3), 1289(8), 1354 (0), 1379 (1*), 1391 (1*), 1421 (8), 1588 (4), 1614 (1*), 1629 (10*), 1658 (1*), 2998 (1**), 3021 (7**), 3051 (1**) 3098 (2*), 3113 (4*), 3128 (2*).

Isoprene, $\Delta\nu$ cm^{-1}: 272 (1*), 285 (2*), 291 (1*), 413 (1**), 421 (3**), 431 (1**), 521 (1*), 529 (6*), 537 (1*), 779 (3 double), 878 (0*), 891 (4* broad), 903 (4* broad), 913 (2*), 955 (5), 996 (3), 1066 (7*), 1072 (2*), 1293 (8** broad, double), 1304 (3**), 1382 (2), 1416 (2*), 1426 (8*), 1437 (2*), 1598 (1), 1623 (0), 1639 (10 broad), 1658 (0), 2865 (0), 2908 (3), 2931 (3), 2982 (2), 3011 (8), 3088 (3).

2,3-Dimethylbutadiene, $\Delta\nu$ cm^{-1}: 383-435 (3, band), 495 (5), 552 (2), 729 (7), 895 (6 broad), 967 (5), 1025(10), 1341 (3), 1381 (5), 1411 (10), 1443 (3), 1470 (3), 1628 (10* broad), 1652 (4*), 1693 (2), 2706 (2), 2736 (2), 2895 (5*), 2917 (10*), 2947 (4*), 2975 (5*), 3007 (7*), 3092 (7).

conformation (IX) should be characterized in Raman spectra by one frequency of the symmetrical vibration of the double bonds (by one frequency of their antisymmetrical vibration in infrared absorption spectra). In the Raman spectra of the liquid phase at room temperature we found intense frequencies for chloroprene at 1588 and 1629 cm^{-1} and for isoprene at 1598 and 1639 cm^{-1}, which belonged to the predominating transoid conformations (VII). The weak frequencies at 1614 (1) and 1658 (1) for chloroprene and 1623 (0) and 1658 (0) for isoprene must have originated from slight traces of forms with the cisoid conformation (VIII) (see Table 2). The absolute predominance of transoid conformations (VII) under these conditions was confirmed chemically: Diels–

*All the Raman spectra of this article were plotted on a home-produced ISP-51 spectrograph and an E-612 Hilger spectrograph.

Alder reactions were readily accomplished under these conditions at an elevated temperature when the transoid conformations (VII) changed into the cisoid conformations (VIII). The Raman spectrum of 2,3-dimethylbutadiene in the liquid phase at room temperature showed three double bond vibration frequencies: an extremely intense one at 1628 cm^{-1} of the double bonds symmetrical vibration in (IX) and two weaker frequencies at 1652 (4) and 1693 (2) of antisymmetrical and symmetrical vibrations of the double bonds in (X) (see Table 2). According to optical data, there was 20-25% of the form with the cisoid conformation in the mixture. In contrast to the other butadienes discussed above, 2,3-dimethylbutadiene undergoes the Diels–Alder reaction comparatively readily in the liquid phase at room temperature and this is apparently explained by the fact that under these conditions quite a considerable amount of the form with the cisoid conformation (X) is present and this promotes this reaction.

The physical constants of the compounds investigated are given below.

	B. p., °C/mm	d_4^{20}	n_D^{20}
cis-1-Chloro-1,3-butadiene (III)	66,8—67°	0,9553	1,4703
Mixture of cis- and trans-1-chloro-1,3-butadienes (III) + (V)	67,2–67,5°	0,9537	1,4712
cis-Piperylene	43,2°/747	0,6923	1,4363
Mixture of cis- and trans-piperylenes (III) + (V)	41,6°/741	0,6772	1,4304
Chloroprene	58,7°/745	0,9585	1,4883
Isoprene	33,4—33,5°/753	0,6760	1,4212
2,3-Dimethyl-1,3-butadiene	67,3°/731	0,7269	1,4385

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*Original Russian pagination. See C. B. translation.

THERMAL DEHYDROGENATION OF 2,5-DIHYDROFURANS

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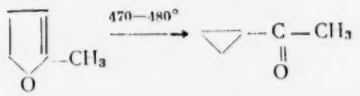
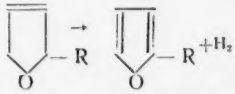
The five-membered heterocyclic compounds tetrahydrofuran, pyrrolidine, and thiophan show considerable differences with regard to their dehydrogenation to the corresponding unsaturated heterocycles. Of these three compounds, pyrrolidine and thiophan may be dehydrogenated to pyrrole and thiophene, respectively, over platinum in the vapor phase at 300-400° [1]. Tetrahydrofuran is not dehydrogenated to furan under the same conditions [2]. However, over a platinum catalyst and in the vapor phase tetrahydrofuran itself and its various homologs undergo isomerization with opening of the ring at one of the C–O bonds with the formation of aliphatic ketones or aldehydes, while the latter are completely decarboxylated to paraffins [3]. In contrast to tetrahydrofurans, dihydrofurans are capable of interesting thermal conversions.

On the example of the conversion of 2,3-dihydrofuran into cyclopropanealdehyde, Wilson [4] demonstrated the possibility of an extremely peculiar conversion from a five-membered oxygen-containing heterocycle to a carbonyl compound of the cyclopropane series. We recently found that 2-methyl-4,5-dihydrofuran undergoes a thermal isomerization of the same type and is converted into methyl cyclopropyl ketone [5].



There is an obvious analogy between the conversions of 2,3-dihydrofurans into cyclopropane carbonyl compounds and the rearrangement of vinyl ethers into aliphatic aldehydes. In connection with these experimental results, there arose the theoretically important problem of the behavior of isomeric 2,5-dihydrofurans at high temperatures. We prepared 2-methyl-2-ethyl-, and 2-isopropyl-2,5-dihydrofurans and investigated their conversions under the conditions under which 2-methyl-4,5-dihydrofuran is isomerized to methyl cyclopropyl ketone, i.e., when the vapors of these compounds were passed over quartz pieces or activated carbon at 470-480°. It was found that under these conditions the 2-alkyl-2,5-dihydrofurans were dehydrogenated very smoothly into the corresponding homologs of furan.



$R = CH_3, C_2H_5,$ iso-C_3H_7.

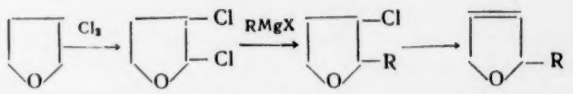
This reaction proceeded about equally readily over quartz and activated carbon (the degree of conversion over quartz was somewhat lower) and this led to the conclusion that the dehydrogenation of 2,5-dihydrofurans to the corresponding furans was not a catalytic reaction, but a thermal reaction occurring at comparatively high temperatures. A temperature of 350° was insufficient for the dehydrogenation of 2,5-dihydrofurans to furans.

The tetrahydrofuran ring did not undergo any changes at 470-480° either over quartz or over carbon. This indicates that the second (conjugated) double bond is formed more readily than the first (isolated) – a phenomenon which has also been observed in other cases.

We should also note another circumstance: The transposition of the double bond from the 3,4-position to the 2,3- or 4,5-position is necessary for the formation of the furan nucleus. However, such systems should be isomerized to cyclopropane carbonyl compounds. As this was not observed, it can be assumed that the transposition of the 3,4-double bond and the elimination of two hydrogen atoms proceed simultaneously without the intermediate formation of a 2,3-dihydrofuran. Thus, the investigation of the thermal conversions of 2,5-dihydrofurans led to the following result: In contrast to 2,3-dihydrofurans, which are isomerized to cyclopropane aldehydes or ketones, 2,5-dihydrofurans are dehydrogenated to the corresponding furans.

EXPERIMENTAL

2,5-Dihydrofurans containing a methyl, ethyl, or isopropyl group in the α position were synthesized according to the following scheme:



The addition of 2-alkyl-3-chlorotetrahydrofurans to potassium hydroxide at 180-200° with immediate distillation of the product gave only 2,5-dihydrofurans in up to 80% yield. The 2,5-dihydrofurans obtained had the following properties:

1) 2-Methyl-2,5-dihydrofuran: b. p. 77-78° (750 mm); n_D^{20} 1.4214; d_4^{20} 0.8826;

2) 2-ethyl-2,5-dihydrofuran: b. p. 103.9-104.5° (750 mm); n_D^{20} 1.4314; d_4^{20} 0.8877;

3) 2-isopropyl-2,5-dihydrofuran: b. p. 122.7-122.9° (750 mm); n_D^{20} 1.4345; d_4^{20} 0.8793.

The vapor of the 2,5-dihydrofurans together with nitrogen was passed through a layer of quartz pieces or activated birch charcoal at 470-480°. The liquid catalyzates, which were obtained in practically theoretical amounts, were distilled in a column. The yields of α-alkylfurans were 90-95%. The following compounds were obtained in a pure form as a result of thermal dehydrogenation:

1) α-Methylfuran: b. p. 62.5-64° (757 mm); n_D^{20} 1.4320; d_4^{20} 0.9118;

2) α-ethylfuran: b. p. 91-91.5° (757 mm); n_D^{20} 1.4404; d_4^{20} 0.9018;

3) α-isopropylfuran: b. p. 107.4-108.4° (745 mm); n_D^{20} 1.4445; d_4^{20} 0.8974.

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SYMMETRY OF COMPLEX COMPOUNDS

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The symmetry of the steric disposition of the ligands around the central ion, determines most of the physicochemical properties of complex compounds. Such properties are, for example, magnetic properties, optical activity, the nature of the infrared spectrum, the number of long wave (electronic) absorption bands, the number of isomers, etc. In the investigation of these properties it is observed that the best agreement with experimental data for most complex compounds is obtained if it is assumed that their symmetry, even in the case of identical ligands, is not the highest possible for the given coordination number [1-4 and others]. This is also confirmed by direct electron and x-ray diffraction measurements [5-7 and others].

Deviations from the highest symmetry, even though they are usually not very great, do not follow directly from existing theories of the formation of a coordination bond, but may be explained in principle on the basis of the theorem on the stability of nonlinear polyatomic molecules proposed by Jahn and Teller [8]. According to this theorem a complex of the type AB_n at the highest symmetry may be found to be unstable, but the methods of the group theory [9] make it possible to find the types of symmetry among which one should look to find a stable configuration for it. Such a qualitative explanation of observed "asymmetries" is of little practical use as it gives no data either on the nature of the deviations from the highest symmetry or on their magnitude. We therefore considered it important to make a quantitative calculation which would give an idea of the actual steric position of the ligands around the central ion and the approximate quantitative characteristics of the deviations of the ligands' positions from the positions of maximum symmetry. The results of this calculation are given in the present communication.

The calculation was carried out as an approximation for ion–ion or ion–dipole interaction between the central ion A and the ligands B. In this approximation, the total (adiabatic) interaction energy $E(R_i)$ in a complex of the type AB_6 with a configuration $A-d^n$ (above a closed shell) and with arbitrary positions of the ligands B may be divided into two parts (with an accuracy up to the constant):

$$E(R_i) = W(R_i) + \varepsilon(R_i). \tag{1}$$

Here $W(R_i)$ is the energy of interaction of the spherically symmetrical residue of the central ion with the ligands and the ligands with each other and $\epsilon(R_i)$ is the mean energy of interaction of the d-electrons with the ligands. The asymmetry of the positions of the ligands is actually caused by the dissymmetry of the φ electron shell of the d-electrons. We therefore consider that only under the influence of a spherically symmetrical closed residue of a central ion would the complex be strictly octahedral with the ligands lying at the points $R'_{0i}(R'_0, \vartheta_{0i}, \varphi'_{0i})$

$$\vartheta_{01} = 0, \quad \vartheta_{06} = \pi, \quad \vartheta_{02} = \vartheta_{03} = \vartheta_{04} = \vartheta_{05} = \pi/2,$$
$$\varphi_{02} = 0, \quad \varphi_{03} = \pi/2, \quad \varphi_{04} = \pi, \quad \varphi_{05} = 3\pi/2.$$

These points, therefore, are the points where

$$\left(\frac{\partial W}{\partial R_i}\right)_{R_i = R'_{0i}} = 0. \tag{2}$$

Our problem consisted of finding the equilibrium positions of the ligands R_{0i} where there is a minimum in the total potential energy $E(R_i)$:

$$\left(\frac{\partial E}{\partial R_i}\right)_{R_i = R_{0i}} = \left(\frac{\partial W}{\partial R_i}\right)_{R_i = R_{0i}} + \left(\frac{\partial \varepsilon}{\partial R_i}\right)_{R_i = R_{0i}} = 0. \tag{3}$$

To find the relation $\epsilon = \epsilon(R_i)$, we assume that the interaction of the ligands with a d-electron

$$V = q \sum_{i=1}^{6} \frac{1}{|r - R_i|} \tag{4}$$

is little disturbed (q is the ion charge; no additional difficulties arise with a change to dipolar ligands).

V is resolved into a series of spherical functions and in the approximation of a central field, with the aid of 5 d-functions

$$\Psi_m = f(r) Y_2^m(\vartheta, \varphi), \quad m = 2, 1, 0, -1, -2, \tag{5}$$

it is easy to obtain the matrix elements:

$$V_{mm'} = q \sum_{i=1}^{6} [A_{mm'} F_4(R_i) Y_4^{m-m'}(\vartheta_i, \varphi_i) + B_{mm'} F_2(R_i) Y_2^{m-m'}(\vartheta_i, \varphi_i) + C_{mm'} F_0(R_i) Y_0^{m-m'}(\vartheta_i, \varphi_i)]. \tag{6}$$

Here

$$F_k(R) = \frac{1}{R^{k+1}} \int_0^R r^k f^2(r)\, dr + R^k \int_R^\infty \frac{1}{r^{k+1}} f^2(r)\, dr, \tag{7}$$

while the constants $A_{mm'}$, $B_{mm'}$, and $C_{mm'}$, are expressed simply through Klebsch–Gordan coefficients.

In the case of a d^1 configuration (central ion of the Ti^{3+} type), the secular determinant of the matrix elements (6) leads to an equation of the 5th order with respect to ϵ. Its solution in a general form can hardly be possible. However, it is possible to make use of the fact that in a field of tetragonal symmetry, the secular equation can be solved accurately. In this case, the lowest levels are either doubly degenerate E with the energy $\epsilon_{12} = V_{11}$, if the tetragonal symmetry is formed as a result of elongation of one of the diagonals of a right octahedron (elongated octahedron), or nondegenerate A_{2g} with the energy $\epsilon_3 = V_{22} - V_{2-2}$, if this symmetry is formed as a result of contraction of the diagonal (contracted octahedron). It is then possible to investigate separately* the behavior of the levels E_g and A_{2g} (in a cubic field they merge into T_{2g}) in a field of arbitrarily placed ligands. The former is divided into two with the energy $\epsilon_{12} = V_{11} \pm |V_{1-1}|$, which gives for the lowest electron term.

$$\varepsilon_1 = V_{11} - |V_{1-1}|. \tag{8}$$

*This is equivalent to neglecting the matrix elements arising from the wave functions of different levels. They are equal to zero for symmetries up to C_{2v}, inclusive.

Substituting (8) in (3) with allowance for (6) and (2) makes it possible to obtain:

$$\vartheta_{01}=0,\quad \vartheta_{06}=\pi,\quad \vartheta_{02}=\vartheta_{03}=\vartheta_{04}=\vartheta_{05}=\pi/2,\quad \varphi_{02}=0,\quad \varphi_{03}=\pi/2,$$
$$\varphi_{04}=\pi,\quad \varphi_{05}=3\pi/2,\quad R_{01}=R_{06}=R_{02}=R_{04},\quad R_{03}=R_{05},$$

where $R_{03} < R_{01}$. Hence, it can be seen that the equilibrium positions of the ligands correspond to tetragonal symmetry,* in which the ligands lie at the vertices of an octahedron contracted along one diagonal. The electronic term will be A_{2g}. The same result is obtained if we start from the level A_{2g} at the very beginning.

It is possible to derive a formula relating the difference in lengths of the diagonals $\xi = 2(R_{01} - R_{03})$ to the force constants of the complex. Considering that ξ is a small parameter, we may resolve E, W, and ϵ into series with respect to ξ and to eliminate all terms above the second order. Then, the conditions for the minimum of total energy (3) gives

$$\xi = \frac{2}{21}\, q\, \frac{5F_4'(R_{01}) - 9F_2'(R_{01})}{k - 2h + l}\,. \tag{9}$$

Here the strokes denote derivatives and $\underline{k}$, $\underline{h}$, and $\underline{l}$ are the force constants of the complex: $\underline{k}$ is the main constant of the elastic bond, $\underline{h}$ is the constant of the "interaction" of two neighboring bonds, and $\underline{l}$ is the constant of the interaction of a bond with the opposite bond ($\underline{h}$ and $\underline{l}$ are small in comparison with $\underline{k}$ so that they can often be omitted). When appropriate values of the parameters are substituted in (9), a value of ξ of the order of 0.5 A is obtained.

If the ligands are not ions, but dipoles with a dipole moment μ, then

$$\xi = -\frac{2}{21}\,\mu\, \frac{5F_4''(R_{01}) - 9F_2''(R_{01})}{k - 2h + l}\,. \tag{10}$$

For AB_6 complexes with the configuration $A-d^9$ (one d-hole in a filled d^{10} shell, i.e., an ion of the Cu^{++} type) it is necessary to investigate the level E_g with the energy $\epsilon = V_{00}$, which is the least in a cubic field. The condition of the minimum to total energy also predicts tetragonal symmetry for these complexes,** but they can be both elongated and contracted octahedra. In both cases

$$|\xi| = -\frac{1}{14}\, q\, \frac{12F_2'(R_{01}) + 5F_4'(R_{01})}{k - 2h + l} \tag{11}$$

for ligands–ions, and

$$|\xi| = \frac{1}{14}\,\mu\, \frac{12F_2''(R_{01}) + 5F_4''(R_{01})}{k - 2h + l} \tag{12}$$

for ligands–dipoles. The order of magnitude of the distortion of the octahedron here is considerably greater (~3 times) than in the case of complexes with d^1 configuration and consequently ξ may reach very considerable values. This, apparently, explains the known structure of the complex $Cu(H_2O)_5SO_4$, in which four water molecules are at considerably shorter distances than the remaining ligands.

For the configuration d^2 (an ion of the V^{3+} type) the wave functions (5) should be correspondingly antisymmetrized. In this case the matrix elements of the secular equation are expressed linearly through the matrix elements (6). In this case also AB_6 complexes are found to be tetragonal and for an elongated octahedron

$$\xi = \frac{1}{70}\, q\, \frac{24F_2'(R_{01}) - 25F_4'(R_{01})}{k - 2h + l}\,. \tag{13}$$

*This result confirms the general conclusions of [10].

**The author recently learned of [11] in which an analogous case was discussed.

However, complexes of the type AB_4 have the highest possible symmetry, i.e., will be right tetrahedra.

For the configuration d^8 (two d-holes, and ion of the Ni^{++} type), the opposite picture is obtained: Complexes of the AB_6 type will have the highest cubic symmetry, i.e., will be right octahedra, while AB_4 complexes will not have the maximum symmetry of a tetrahedron, but will be tetragonal with the planar structure of a square. These conclusions are confirmed by voluminous experimental data.

It should be noted that the conclusions we reached on the symmetry of complexes are of general significance, which does not depend on the type of bond in them. As regards formulas (9)-(13), they may be used for quantitative characterization of the distortion of the highest symmetry in a complex only as far as the actual bonds in it approach an electrostatic bond; to the same extent they may be used for calculating the force constants if the distances between the central ion and the ligands have been measured.

In conclusion I would like to express my sincere thanks to A. V. Ablov, M. G. Veselov, Yu. E. Perlin, and T. I. Malinovskii for valuable discussions.

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KINETIC CHARACTERISTICS OF THE LIQUID-PHASE AUTOOXIDATION OF ISOPROPYLXYLENES

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As was shown previously [1], the autooxidation of polyalkylbenzenes which do not contain alkyl groups in positions ortho to each other is a strictly successive reaction.

In a continuation of this investigation it seemed interesting to study the kinetics of the autooxidation of polyalkylbenzenes with substituents lying adjacent. The following compounds were chosen: o-xylene (I), 4-isopropyl-o-xylene (II), 3-isopropyl-o-xylene (III), 2-isopropyl-p-xylene (IV), 4-isopropyl-m-xylene (V), 2,5-diisopropyl-p-xylene (VI), and o-cymene (VII).

It was established that together with the usual products (alcohols, ketones, acids, etc.), the autooxidation of all these hydrocarbons yielded also γ-lactones – phthalide derivatives. We were the first to observe the formation of the latter under liquid-phase autooxidation conditions.

At 120° and in the presence of 0.6 mol. % of cobalt acetate, 60-70% of (I) was oxidized after 8-10 hr. In addition to the main reaction product, o-toluic acid, 5-8% of phthalide and 2-5% of a mixture of tolualdehyde and tolylcarbinol were formed. The maximum hydroperoxide concentration did not exceed 1-1.5%. Quite a complex mixture was formed when (II) was oxidized. In the early stages of the autooxidation, the isopropyl group reacted with peroxide radicals 1.8-2.1 times faster than the two methyl groups. Of the latter, the radical para to the isopropyl group was oxidized about 1.2 times more readily. The effect of various factors on the course of the oxidation of (II) is given in Table 1. As the data in Table 1 show, the yield of lactones was approximately 5% of the hydrocarbon oxidized. Other products with two oxidized groups (acetyl-α-hydroxyisopropyltoluic acids etc.), were formed in appreciable amounts when the degree of oxidation was more than 30%.

TABLE 1

Autooxidation of 4-isopropyl-o-xylene

Expt. No.	Reagents taken per M hydrocarbon: manganese resinate, mg	Reagents taken per M hydrocarbon: soda, g	Temp. °C	Hydroperoxide conc., % (above line), time in hr (under line)	Composition of reaction mixture after reduction of peroxides with Na_2SO_4, mol. %: hydrocarbon	dimethylxylylcarbinol	dimethylacetone	isopropyltoluic acids	isopropylcarbinols	isopropylphthalide	other products with two oxidized groups
1	10	1.5	120	8,4/1; 18,0/4; 16,5/6	66,4	14,1	6,3	5,5	6,0	1,0	0,7
2	6	3,0	110	12,5/2; 29,0/6; 23,0/9	51,2	22,8	6,9	11,5	2,5	2,2	2,9
3	4	3,5	110	9,4/1; 15,1/2	82,8	11,3	0,2	1,9	3,2	0,6	—
4	5	4,0	100	5,3/3; 12,0/7; 16,3/10	71,8	13,8	—	2,3	3,6	0,5	—
5	170	—	110	7,0/1; 4,02; 1,2/4	21,5	24,6	21,0	17,1	6,2	4,1	5,6

Footnote. Cobalt acetate was used in experiment 5.

The autooxidation of hydrocarbons (III)-(VII), which have adjacent methyl and isopropyl groups, was most interesting. Hydrocarbons (III)-(V) were oxidized very slowly in the presence of manganese resinate. The use of cobalt acetate and isopropyltoluate as initiators considerably accelerated the oxidation, but it was not possible to direct the process predominantly toward the formation of peroxides as the latter decomposed very rapidly in the presence of cobalt salts. In the presence of 6 mg/mole of manganese resinate and 10 mg/mole of soda it was possible to oxidize (VI) to a 10% hydroperoxide concentration after 7 hr at 110°.

While in (II) the isopropyl group was oxidized almost 4 times more readily than the methyl group, in (IV) and (V) the total rate of oxidation of the two adjacent groups was only 1.3-1.7 times that of the isolated methyl group due to steric hindrance. It is interesting to note that the oxidation of p-xylene at 120° was only a factor of 1.3 worse than that of(IV). (The ratio of the rates was established by combined oxidation of the hydrocarbons.)

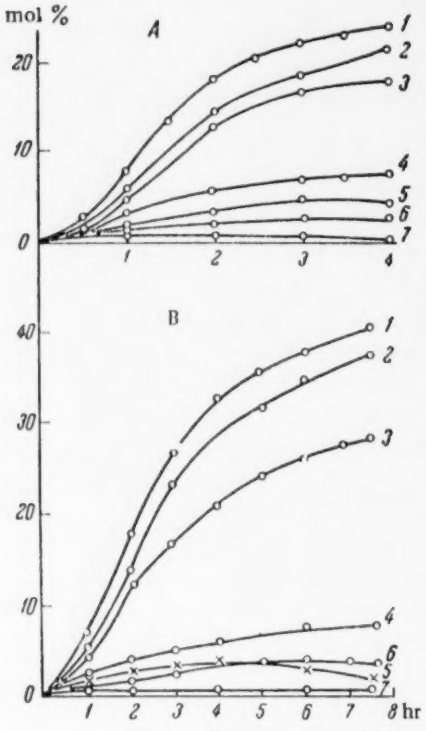


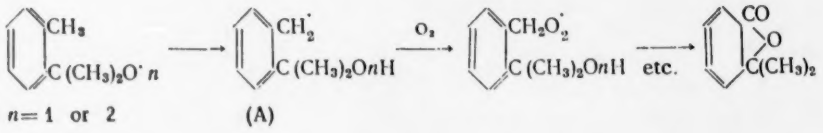
Fig. 1. Kinetics of the accumulation of oxidation products of V (A) and IV (B): 1) acids; 2) total amount of lactones; 3) trimethylphthalide; 4) ketones; 5) primary alcohols; 6) tertiary alcohols; 7) hydroperoxides.

Figure 1 shows the kinetics of accumulation of products from the oxidation of 4-isopropyl-m-xylene (V) at 130° in the presence of 1 mol. % of cobalt isopropyltoluate with an air input rate of 1 liter/min and of 2-isopropyl-p-xylene (IV) at 160° with 1 mol. % of cobalt isopropyltoluate and an air input rate of 1 liter/min. The composition of the oxidation products of (IV) and (V) for some experiments is shown in Fig. 1 and Table 2. These data show that lactones were formed at a considerable rate even in the very early stages of the reaction.

More than 50% of lactones was formed during the oxidation of (VI). High yields of lactones were also obtained during the oxidation of diisopropyl-m-xylenes, (III) and (VII). If the oxidation of these hydrocarbons proceeded as a normal successive process, then, as is readily shown by kinetic equations [1], the formation of such large amounts of lactones would only be possible when the rate of oxidation of the second group was many times greater than the rate of oxidation of the hydrocarbon. However, by special experiments we established that substances with one oxidized alkyl group, further oxidation of which could yield lactones, were less reactive than the hydrocarbon. The addition to (IV) of dimethyl-p-xylylcarbinol (VIII), 2-acetyl-p-xylene (IX), a mixture of isopropyl-p-toluic acids, and other products isolated from the reaction mixture did not increase the yield of lactones appreciably.

The oxidation of a mixture of (VIII), (IX), and p-xylene showed that the rates of oxidation of these compounds were similar. In addition, it was noted that the yield of lactones did not increase symbatically with the concentration of hydroperoxides.

All that has been stated indicates that the main reason for the formation of high yields of lactones is isomerization of free radicals. For example:



$n = 1$ or 2 (A)

Since a radical of the benzyl type (A) can hardly abstract a hydrogen atom from surrounding molecules as the latter reaction for similar radicals proceeds 10^5-10^6 times more slowly than the addition of oxygen [2], almost each isomerization act must lead to the formation of products with two neighboring oxidized groups.

In addition to derivatives of 3,3-dimethylphthalide, the oxidation of (III)-(VII) also yielded other substances whose chemical properties were identical with those of phthalides. We were unable to isolate them in the form of individual compounds. However, there is no doubt that these substances were obtained as a result of autooxidation of two neighboring alkyl groups as on oxidation with alkaline $KMnO_4$, they gave 4-methyl-o-phthalic acid. By autooxidation of (IX) we also obtained compounds of the lactone type in a yield of 20-28% of the oxidized product.

EXPERIMENTAL

Isopropylxylenes were obtained by alkylation of appropriate xylenes with propylene in the presence of $BF_3 \cdot H_3PO_4$ or with isopropyl alcohol in the presence of 85% H_2SO_4. (VIII) was obtained by the Grignard reaction from 2-bromo-p-xylene and (IX) was synthesized from p-xylene and acetyl chloride in the presence of $AlCl_3$. The starting xylenes were chemically pure commercial preparations. The hydrocarbons were carefully purified by fractionation in a column of 25-30 theoretical plates and had constants corresponding to literature data. (VII) was used as a mixture of isomers which contained about 40% of o-cymene.

The autooxidation was carried out as previously [1], but a graduated trap was used to determine the amount of water liberated. During the reaction samples were taken for determination of the contents of hydroperoxides, acids, primary and tertiary alcohols, unsaturateds, ketones, keto acids, and lactones. The determination of the lactones was based on the fact that when the alkali salts of the hydroxy acids obtained by hydrolysis were heated in an acid or even weakly alkaline medium, they were quantitatively converted into neutral lactones. (Derivatives of 3,3-dimethylphthalide were formed readily in a weakly alkaline medium, while phthalide and related compounds were formed in an acid medium.)

The tertiary alcohols were determined by dehydration in the presence of $KHSO_4$ with subsequent titration of the water with Fischer's reagent. The remaining compounds were determined by the normal methods. When titration with indicators was difficult, potentiometric titration was used.

The composition of the isomeric isopropyltoluic acids was established in the following way. The acids were decarboxylated almost quantitatively in the presence of copper powder in quinoline and the mixture of cymenes was oxidized with a dilute HNO_3 in an autoclave to phthalic acids, which were separated through the barium salts or by means of their different solubilities in water. It was thus established that the oxidation of (II) yielded about 55% of 4-isopropyl-o-toluic acid (m. p. 89°) and 45% of 5-isopropyl-o-toluic acid. The mixture

TABLE 2

Autooxidation of 2-Isopropyl-p-xylene and 4-Isopropyl-m-xylene

Experiment No.	Cobalt isopropyltoluate taken, mol. %	Temp., °C	Hydroperoxide concentration, %(above line), time in hr (below line)	Reaction time, in hr	Yield of oxidation products on hydrocarbon taken, mol. %						Hydrocarbon regenerated (mol. %)
					trimethylphthalides	other lactones	isopropyltoluic acids	dimethylxylylcarbinol	dimethylacetophenone	isopropyltolylcarbinols	
1		110	1,2/5; 3,5/12; 1/24	24	4,8	0,8	8,3	2,9	2,0	2,6	70,2
2	0,6	110	2,0/1; 3,8/3; 1,6/9	9	14,0	2,1	29,5	4,2	3,5	5,0	46,5
3	1,5	115	1,3/4; 1,7/6; 0,5/14	14	12,6	3,0	25,8	2,7	4,1	3,3	42,0
4	1,0	125	0,6/1; 0,9/2	2	5,1	1,2	4,3	2,9	1,8	1,9	77,6
5	1,0	160	0,3/1; 0,4/3; 0,3/7	7,5	18,1	7,5	27,0	2,5	6,7	1,7	21,0
6	1,2	140	0,4/2; 0,5/3,5	3,5	15,2	4,0	21,2	3,2	5,9	4,1	39,0

Footnote. 1. (IV) was oxidized in experiments 1-4 and (V) in 5-6. 2. In experiment 1, 10 mg/mole of manganese resinate and 3 g/mole of soda were used.

of acids obtained by oxidation of (IV) and (V) contained respectively 80% of 3-isopropyl-p-toluic acid (m. p. 147°) and 75% of 4-isopropyl-m-toluic acid (m. p. 128°). There was approximately the same ratio between the isomeric isopropylxylylcarbinols, which were isolated from the mixture through the esters and converted into acids or directly into cymenes by heating with potassium hydroxide [3].

The acids were isolated from the reaction mixture by means of soda (the lactones did not dissolve in soda). Various methods were used in the isolation of the lactones (extraction with caustic alkali, rectification, and recrystallization). We were able to obtain the following lactones in a pure form and identify them. Phthalide (X) with m. p. 75°; 3,3-dimethylphthalide (XI) with m. p. 69.5°; 3,3,5-trimethylphthalide (XII) with m. p. 92° and b. p. 297°; 3,3,6-trimethylphthalide (XIII) with b. p. 294° n_D^{20} 1.5280, d_4^{20} 1.087; 3,3,7-trimethylphthalide (XIV) with m. p. 60.5°; 3,3,5-trimethyl-6-isopropylphthalide (XV) with m. p. 85° and b. p. 165°/10 mm.

Mixed melting points of (X) and (XI) with authentic samples were not depressed. The structures of (XIII) and (XIV) were demonstrated by their oxidation with alkaline $KMnO_4$ to acids. 3,3-Dimethylphthalide-6-carboxylic acid had m. p. 204° and 3,3-dimethylphthalide-7-carboxylic acid had m. p. 185°, which correspond to literature data [4, 5]. (XII) was oxidized with nitric acid to trimellitic acid and converted by heating with KOH into p-toluic acid and acetone.

The structures of the dimethylacetophenones were confirmed by preparation of simicarbazones and 2,4-dinitrophenylhydrazones. The tertiary alcohols could not be isolated in a pure form. Their structures were demonstrated by conversion into the corresponding trimethylstyrenes, which we oxidized with permanganate to dimethylacetophenones or dimethylbenzoic acids.

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OXIDATION OF CYCLOHEXANOL WITH OZONIZED OXYGEN

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Gas initiation of liquid-phase oxidations was proposed and achieved by N. M. Emanuel' et al., [1-3]. The present work was devoted to the study of cyclohexanol oxidation by ozonized oxygen. The results of the work shed light on the mechanism of the ozone oxidation of aliphatic compounds in the liquid phase.

The experiments were carried out in the following way. Cyclohexanol (25-30 ml) was oxidized in a glass reactor with oxygen containing 0.3 ± 0.3% of ozone bubbled through at a rate of 6.7 ± 0.7 liter/hr at 50-100°. During the oxidation samples of oxidized cyclohexanol were taken and analyzed for cyclohexanone, peroxides, acids, and esters. During the experiment, the ozone concentration before the reactor and after it was determined systematically by means of KI. Cyclohexanone, hydrogen peroxide, adipic acid, and esters were formed as a result of the oxidation. The accumulation of cyclohexanone and peroxide at the beginning of the reaction was linear, and at an appreciable degree of oxidation (~10%) the concentrations of ketone and peroxide passed through a maximum. Table 1 gives data on the composition of the products after 2-hr oxidation. The composition of the products from thermal oxidation with ozonized oxygen at 120° was remarkable for the high content of acids and esters (10-20% instead of 1-2%). Comparison of the amount of ozone absorbed with the oxygen content of the oxidation products shows (Table 1) that at 50°, oxygen was not involved in the oxidation, but at higher temperatures it was undoubtedly involved in the reaction. In the calculation it was assumed that all three oxygen atoms of the ozone absorbed passed into the oxidation products.

TABLE 1

Yield of Products and Oxygen Consumed during the Oxidation of Cyclohexanol with Ozone

Temp. °C	Comp. of oxidation products, mol. %			Yield of products on O_3 absorbed, mol.%	O_2 consumed per molecule of O_3 absorbed
	peroxide	ketone	acid+ester		
50	51	64	36	137	—0,04
60	49	55	45	173	0,33
70	73	73	27	190	0,45
80	51	84	16	310	0,94
	54	80	20	310	1,03
90	61	83	17	333	1,13
100	69	69	31	290	1,25

TABLE 2

Rate of Initiation of Chains and Their Length during the Oxidation of Cyclohexanol with Ozone

Temp., °C	v	$v-v_{O_3}$	v_ν (calc.)	W_0	ν
	10^{-6} mole/liter·sec				
50	11	0,0	1,1	0,003	370
60	12,5	1,5	2,0	0,005	400
70	12	1,0	4,0	0,009	450
80	19	8	6,3	0,012	520
90	23	12	10	0,016	620
100	27	16	16	0,025	640

The fact that oxygen was involved in the reaction indicates the chain mechanism of the oxidation. To check this hypothesis we carried out experiments with an inhibitor (hydroquinone) introduced into the oxidation reaction. The oxidation of cyclohexanol by ozonized oxygen was retarded by 10-40 mmole/liter of hydroquinone. The retardation was incomplete at 50-60°, but at higher temperatures the reaction practically stopped for some time (Fig. 1). A comparison of the oxidation by ozone with thermal oxidation showed that the inhibitor was mainly consumed by reaction with ozone. Therefore, the rate of its consumption could not be used for determining the rate of initiation of chains. Although experiments with the introduction of inhibitor demonstrated the presence of a chain mechanism, they did not answer the question of whether the whole of the cyclohexanol was oxidized by a chain mechanism or only a certain part of it. The results of our work on the thermal oxidation of cyclohexanol helped to solve this problem. The rate of chain oxidation is given by the equation:

$v_\nu = \frac{k_2}{\sqrt{k_6}}[RH]\sqrt{W_0}$, where k_2 and k_6 are constants referring to the reactions $RO_2 + RH$ and $RO_2' + RO_2'$, respectively. The activation energy for the rate $v_\nu E = E_2 + {}^1/_2 E_0 > E_2 = 7.7$ kcal/mole. Let us assume that cyclohexanol is oxidized only by a chain mechanism. From experiment we know that at 50°, $v = 11 \cdot 10^{-6}$ mole/liter · sec and at 100° $v = 27 \cdot 10^{-6}$ mole/liter · sec. This change in v with temperature corresponds to E = 4 kcal/mole. But E ought to be > 7.7. Thus, the facts that oxygen is involved in the oxidation and the retardation of the reaction by an inhibitor indicate that the reaction has a chain mechanism, while the assumption that the reaction is only a chain reaction is contradicted by data on the thermal oxidation of cyclohexanol. It must be assumed that cyclohexanol is oxidized by ozonized oxygen by two mechanisms: a chain mechanism with rate v_ν and a non-chain mechanism with rate v_{O_3} equal to the rate of introduction of ozone into the reactor. v_{O_3} is independent of temperature. At low temperature $v \approx v_{O_3}$ but v_ν increases with a rise in temperature (see Table 2).

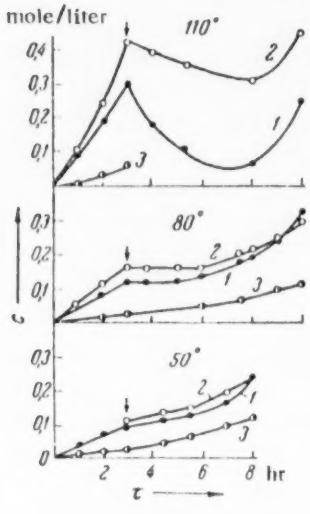


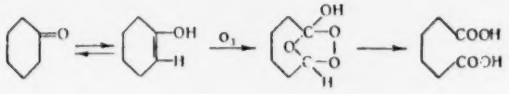
Fig. 1. Kinetics of the oxidation of cyclohexanol by ozonized oxygen with an inhibitor introduced during the reaction (the moment of introduction is marked with an arrow). 1) Hydrogen peroxide; 2) cyclohexanone; 3) acids.

The temperature dependence of v_ν corresponds to an activation energy E = 13 ± 2 kcal/mole, which agrees well with thermal oxidation data. Together with v_ν from experiment, we give the values of v_ν calculated from the value of v_ν at 90° C and E = 13 kcal/mole. As $v_\nu = k_2/\sqrt{k_6}(RH)\sqrt{W_0}$ and $k_2 k_6^{-1/2} = 320\, e^{-7700/RT}$ (from experiments on the thermal oxidation of cyclohexanol), then it is possible to find the rate of chain initiation $W_0 = v_\nu^2 k_6 / k_2^2 (RH)^2$ and $\nu = v_\nu / W_0$. These values are given in Table 2, which shows that $W_0 \approx 10^{-8}$ mole/liter sec and $\nu \approx 400$-600 and that W_0 and ν increase with a rise in temperature. This leads to the fact that v_ν becomes greater than v_{O_3} with a rise in temperature. If W_0 is compared with the rate of admission of ozone to the reactor, it is found that only 0.1% of the ozone is consumed in the initiation of chains and that practically all of the ozone reacts with cyclohexanol without the formation of free radicals. W_0 is small because ozone reacts very rapidly with cyclohexanol and its concentration is low. The ozone concentration may be evaluated in the following way. Let us assume that the Henry coefficient for the solution of ozone in the alcohol is the same as that for oxygen, i.e., 10^{-2} mole/liter · atm. The partial pressure of O_3 at the reactor outlet equaled 10^{-4} atm and hence $[O_3] \approx 10^{-6}$ mole/liter.

The activation energy of chain initiation by ozone $E_0 = 2(E - E_2) = 2(13-7.7) = 11$ kcal/mole. Consequently, the initiation of chains by the decomposition of an ozone molecule to an atom and a molecule of oxygen does not play any appreciable role as in this case, E_0 would be close to 25 kcal/mole. The formation of free radicals in the liquid phase apparently proceeds by a bimolecular reaction of O_3 and RH: $RH + O_3 \rightarrow R^{\cdot} + HO^{\cdot} - q$, for which $E_0 \approx q = Q - 100 + 25 = Q - 75$, where Q is the energy of rupture of the R–H bond. For cyclohexanol Q < 90 and hence $E_0 < 15$, which agrees well with the value $E_0 = 11$ kcal/mole from experiment. The rate constant of chain initiation with the assumption that $[O_3] = 10^{-6}$ mole/liter is given by $k = 6 \cdot 10^3\, e^{-11000/RT}$ liter/mole · sec.

Interesting data were obtained by us on the mechanism of the reaction of ozone with cyclohexanone. When inhibitor was introduced at 100°, there was a decrease in the cyclohexanone concentration, which indicates

a nonchain mechanism for the reaction of ozone with cyclohexanone (it is consumed only by a chain mechanism in the thermal oxidation). A special experiment on the oxidation of cyclohexanone by ozonized oxygen at 80° with the introduction of inhibitor showed that cyclohexanone is oxidized by a nonchain mechanism with the formation of acids (the inhibitor did not retard the reaction). It is possible that the oxidation proceeds through the reaction of ozone with the enol form of the ketone.



In the oxidation of cyclohexanol at 80° the maximum ketone concentration was 0.75 mole/liter and hence it follows that ozone reacts with cyclohexanone 20 times faster than with cyclohexanol.

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*Original Russian pagination. See C. B. translation.

ABSORPTION SPECTRA OF NITROBENZENE SOLUTIONS OF DIMETHYLAMINOSTYRYL DERIVATIVES OF ACRIDINE

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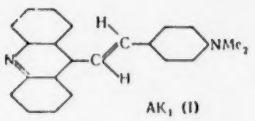
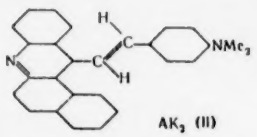
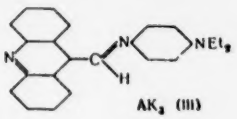
Dimethylamine derivatives of quinoline and acridine (electron-donor components of the type AK*) may form colored molecular complexes of the type [BK⌢AK] with quinolinium and acridinium electrophilic components of the type BK* [1-4]. Considering the capacity of aromatic amines to give molecular complexes with nitrobenzene (BK component) [5-7], it may be presumed that similar colored complexes with nitrobenzene should be formed by dimethylaminostyryl derivatives of acridine and quinoline. In order to check this hypothesis we studied the spectra of solutions of molecular complexes formed by solution in nitrobenzene of a number of components AK_1-AK_5 (I-V), which were anhydro bases of acridine derivatives (Table 1**).



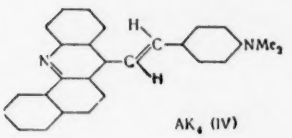
AK_1 (I)



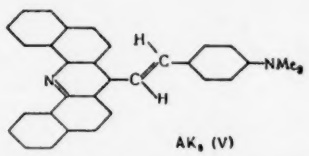
AK_2 (II)



AK_3 (III)



AK_4 (IV)



AK_5 (V)

To displace the equilibrium AK + BK ⇌[AK⌢BK] toward complex formation, we used a large excess of nitrobenzene (BK) as solvent. In all cases the reaction of the AK components given above with $C_6H_5NO_2$ (BK) led to a bathochromic displacement of the curve of the anhydro base, which we explained by the formation of a complex in solution.

We made the following observation, which is of very great importance from our point of view: In the formation of complex $C_6H_5NO_2$ with 9-(p-dimethylaminostyryl)-acridine (AK_1, I) (2, Fig. 1) or with

*AK and BK are complex chromophoric components made up from an electron-donor chromophoric component A (for example, NMe_2) or, correspondingly, an electrophilic chromophoric component B (for example, C=N or NO_2) with a π-electron conjugated system K.

**λ_{max} and ϵ determined approximately from an inflection in the curve are denoted by the sign ⌢. The values of ϵ for solutions of the complexes are only arbitrary values [5] which may be used for comparing the degrees of complex formation.

9-(p-dimethylaminostyryl)-3,4-benzacridine (AK_4, IV) (11, Fig. 2) a new band appeared, which in form and the region of its maximum was remarkably close to the long wave band and the λ_{max} of the corresponding dyes (3, Fig. 1, and 12, Fig. 2) formed by addition of HCl and RX to the anhydro base, and of the corresponding complex from the AK compounds mentioned with the acridinium component BK [2-4]. This indicates that $C_6H_5NO_2$

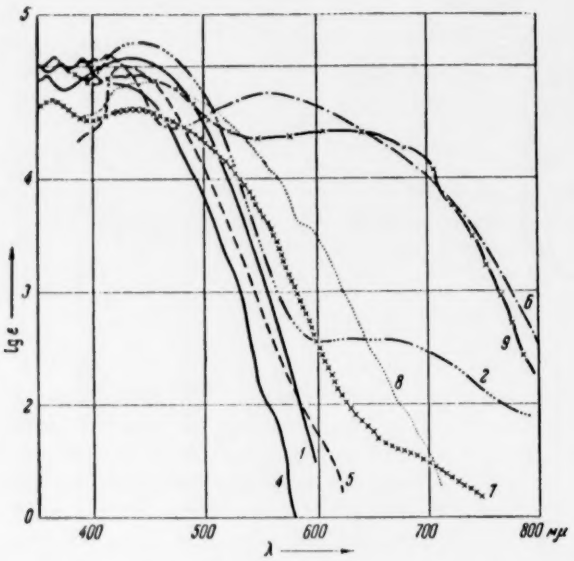


Fig. 1. Absorption spectra of molecular complexes from AK_1, AK_2, and AK_3 with nitrobenzene. The numbers of the curves correspond to the numbers of the solutions in Table 1. 3) λ_{max} 616 mμ (ϵ = 29810) [2].

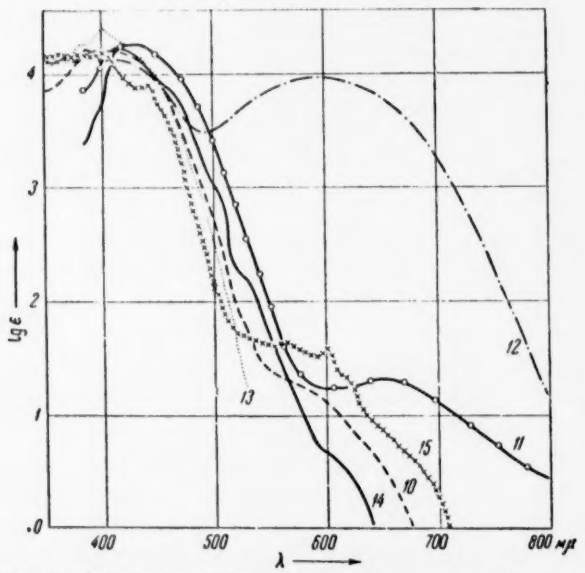


Fig. 2. Absorption spectra of molecular complexes from AK_4 and AK_5 with nitrobenzene. The numbers of the curves correspond to the numbers of the solutions in Table 1.

TABLE 1

Comparison of Absorption Spectra of Components of the Type AK with Spectra of Molecular Complexes of the Type [AK⌢BK] and the Corresponding Dyes B–K–A

Sample No.	Symbol and component ratio	Solvent	C, mole/liter	Absorption bands of dye and complex		Absorption bands of components	
				λmax	ϵmax	λmax	ϵmax
1	AK_1 (I)	C_2H_5OH	10^{-3}	—	—	434	12500
2	$1AK_1{:}{\infty}BK$	$C_6H_5NO_2$	10^{-3}	621	39	443	16400
3	$A{-}K_1{-}B$ [1]	C_2H_4OH [3]	10^{-3}	614	29810	356	20940
4	AK_2 (II)	C_2H_5OH	10^{-3}	—	—	389	12080
5	$1AK_2{:}{\infty}BK$	$C_6H_5NO_2$	10^{-3}	~585	~10	425	10200
6	$A{-}K_2{-}B$ [2]	DCE [3]	10^{-3}	561	5850	415	12370
7	AK_3 (III)	$CHCl_3$	10^{-2}	—	—	430	4140
8	$1AK_3{:}{\infty}BK$	$C_6H_5NO_2$	10^{-3}	~585	~400	450	7550
9	$A{-}K_3{-}B$	AK_3 [4]	10^{-3}	625	2715	440	8535
10	AK_4 (IV)	$CHCl_3$	10^{-2}	—	—	416	17720
11	$1AK_4{:}{\infty}BK$	$C_6H_5NO_2$	10^{-3}	648	20	430	19300
12	$A{-}K_4{-}B$ [5]	DCE [3]	10^{-3}	599	9910	388	17290
13	AK_5 (V)	DCE [3]	10^{-3}	—	—	401	25360
14	$1AK_5{:}{\infty}BK$	$C_6H_5NO_2$	10^{-3}	~590	~7	420	17750
15	$A{-}K_5{-}B$	AK_5 (V) [6]	10^{-3}	600	38	403	16200

[1] AK_1 (I) in 0.01 N HCl in EtOH [2].
[2] Ethylperchlorate of AK_2.
[3] 1,2-Dichloroethane.
[4] AK_3 (III) in 0.001 N HCl in $CHCl_3$.
[5] Ethylperchlorate of AK_4.
[6] AK_5 (V) in 0.01 N HCl in $CHCl_3$.

is present in the complex as an aprotonic acid. An explanation for the above-mentioned similarity of the curves and absorption regions of the complexes with $C_6H_5NO_2$, with the acridinium BK component, and with the corresponding dye may be sought in the ionization of the complex on formation [6]. Another explanation is more probable. This is that the transfer of charge on excitation by light occurs not between the components forming the complex [7], but in one of the components, AK in the given case, which acquires a partial charge (δ^+) [8] as a result of complex conjugation ("complex mesomerism") [9, 10]. * Thus, in the complexes mentioned the systems AK_1 and AK_4 play the part of the main chromophoric component.

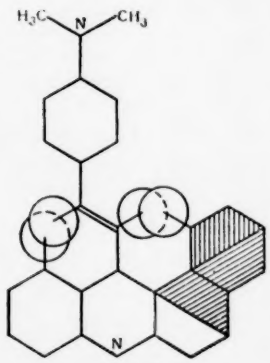


Fig. 3.

A comparison of the spectra of solutions 1 and 3 with those of solutions 4 and 6 (Table 1, Fig. 1) shows that the elimination of the benzene ring in the 1,2-position in 9-(p-dimethylaminostyryl)-1,2-benzacridine (AK_2, II) leads to a sharp hypsochromic displacement of the curve in comparison with (AK_1, I) both for the anhydro base (4) and for the dye salt (6) (N-ethyl perchlorate of AK_2 (II)). The reason for this could be dissipation (as a result of the elimination) of the conjugation effect (meso effect) [13] in the ground state and on conversion to the excited state. However, the main reason should be considered the departure from coplanarity of the dimethylaminostyryl chromophoric group and the cross-hatched parts of the molecule in Fig. 3, as may be conjectured in analogy with benzo[c]phenanthrene (x-ray structural data [14]). These phenomena are reflected to an even greater degree by the spectrum of the solution of (AK_2 + $C_6H_5NO_2$). In the visible region of the spectrum there was only a slight displacement of the curve toward longer wavelengths (at $\lg\epsilon = 1\ \Delta\lambda = +30$ mμ) and the characteristic band in the region of 600-700 mμ (observed in the case of 2 and 11) was absent and there was only a weakly expressed inflection (5, Fig. 1).

* The concept of "complex mesomerism" ("complex resonance") was put forward much earlier by Brackman [11] and Mulliken [12].

Replacement of the CH=CH group in (I) by the CH=N group in the p-diethylaminoanil of acridine-9-aldehyde (AK_3, III) with the simultaneous replacement of the NMe_2 group by NEt_2* produced in the anhydro base (III) a bathochromic displacement of the long-wave section of the curve (at $\lg \epsilon = 1$ $\Delta\lambda = +42$ mμ).

For a solution of (III) in nitrobenzene there was only a bathochromic displacement of the curve with an inflection at ~590 mμ (8, Fig. 1). The displacement appeared to an even stronger extent with the dye (hydrochloride of AK_3, Fig. 1, 9). Analogous phenomena were observed for the first time by A. I. Kiprianov [16]. A similar phenomenon was also observed later [17]. Unfortunately, the isomer with the reversed group, i.e., an azomethyne group N=CH is inaccessible due to the tautomeric structure of 9-aminoacridine.

In the case of 9-(p-dimethylaminostyryl)-3,4,5,6-dibenzacridine AK_5 (V) the presence of two condensed benzene nuclei leads to even greater dissipation of the conjugation effect. The spectra of the anhydro base and a solution of (V) in nitrobenzene showed a strong hypsochromic displacement. For the molecular complex $[AK_5 \frown C_6H_5NO_2]$ we found λ_{max} ~590 mμ, for an inflection which almost coincided with λ_{max} 600 mμ for the hydrochloride of AK_5 (Fig. 2, 14 and 15).

The extremely low values of ϵ (2, 5, 8, 11, 14, Table 1) of the order of 20-40 were considerably lower than the values of ϵ we observed for solutions of the complexes of α- and β-naphthylamines with nitrobenzene (ϵ = 1620 and 208, respectively [18]). We explain this by the fact that the anhydro bases (I-V) contain the grouping $\overset{\delta+}{C} = \overset{\delta-}{N} -$, which leads to an increase in the conjugation of NMe_2 (in the dimethylaminostyryl grouping) and hence a decrease in the basicity and the capacity of the AK system to react with $C_6H_5NO_2$. The grouping $\diagdown C = N - \diagup$ is absent from the molecules of α- and β-naphthylamines. An investigation of the possibility of replacing the acridinium or quinolinium component by nitrobenzene in "donor-acceptor" complexes gave a new demonstration of the fact that the appearance of color when a complex is formed is not connected with alcoholysis of the onium component and the formation of halochromic adducts with the AK component (for other demonstrations see [2, 3, 4, 7]).

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*We were obliged to do this to increase the solubility [15].

**Original Russian pagination. See C. B. translation.

NEW REARRANGEMENT OF TRIHALOACETHYDROXAMIC ACIDS

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α-Halogenated aliphatic hydroxamic acids are compounds which have been studied little. Only monochloro- [1], dichloro- [2], monobromo- [1], and monoiodoacethydroxamic acids [1] have been described. Trichloroacethydroxamic acid has been isolated only in the form of its salt with hydroxylamine [1]. α-Fluoro aliphatic hydroxamic acids are unknown.

Fluorine- and chlorine-substituted acethydroxamic acids are readily formed by the reaction of esters of appropriate haloacetic acids with free hydroxylamine in absolute alcohol. In this way we prepared monofluoro-, trichloro-, fluorodichloro-, and trifluoroacethydroxamic acids, which were colorless, hygroscopic, crystalline substances that were readily soluble in water, alcohols, and acids and sparingly soluble in most organic solvents.

It is interesting to note that aqueous solutions of trifluoroacethydroxamic acid showed a variable basicity, depending on the period of their storage. This change in the basicity of dilute aqueous solutions of trifluoroacethydroxamic acid with time is shown in Fig. 1. In connection with this we may assume the existence of a dynamic equilibrium of two tautomeric forms of trifluoroacethydroxamic acid with a dilute aqueous solution containing not less than 37% of the dibasic form.

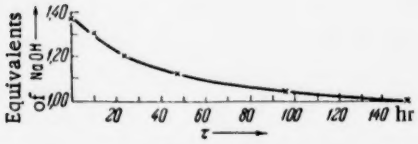
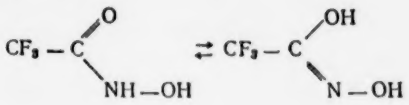


Fig. 1.



It is known that most hydroxamic acids and also their salts and acyl derivatives are characterized by a tendency to undergo a Lossen rearrangement with the formation of corresponding isocyanates or their conversion products (amines, substituted ureas, and urethans). The rearrangement of halo-substituted acethydroxamic acids has been studied previously only on the examples of the thermal decomposition of dichloroacethydroxamic acid and its benzoate [2]. In both cases it was impossible to isolate dichloromethyl isocyanate or its normal conversion products. The hypothesis was put forward [3] that the initially formed isocyanate was converted into dichloromethylamine, which was dehydrochlorinated with the liberation of hydrocyanic acid.

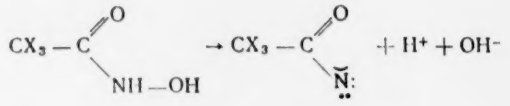
In connection with this it may be assumed that the rearrangement of other halo-substituted acethydroxamic acids should also proceed according to the general type of Lossen reaction with possible subsequent conversion of the isocyanates.

In order to check this hypothesis, we studied the thermal decompoeition of trichloro- and trifluoroacethydroxamic acids. It was found that when these compounds were heated above their melting points there was vigorous decomposition and trichloro- or trifluoronitrosomethane and formaldehyde were unexpectedly formed as the main reaction products.

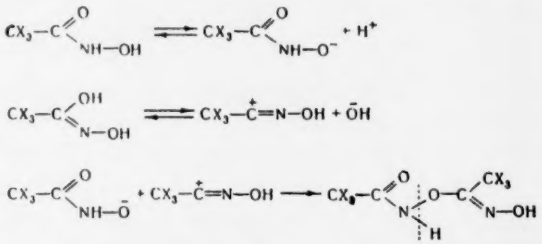
$$CX_3 — CO — NH — OH \rightarrow CX_3NO + CH_2O.$$

Simultaneously with this, small amounts of hydrocyanic acid and carbon dioxide were liberated.

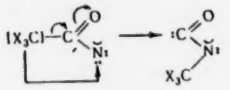
The formation of nitroso compounds during the decomposition of hydroxamic acids has not been observed previously. It is evident that in this case, due to the peculiar distribution of electron density in molecules of fully halogenated hydroxamic acids and their intermediate conversion products, there is a rearrangement which differs from the Lossen reaction. It may be assumed that the initial stage in this rearrangement is the formation of an "azacarbene" derivative [4]:



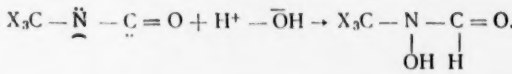
The generation of the latter is apparently facilitated by the acid–base dissociation of hydroxamic acids.



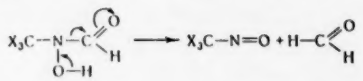
Subsequent stabilization of the "azacarbene" is achieved by transfer of a trihalomethyl cation with the formation of a new nitrogen–carbon bond due to coordination of one of the unshared electron pairs of the nitrogen atom.



The dipolar ion formed is hydrated and the order of addition of the elements of water is found to be the reverse of the direction of hydration of isocyanates.



The latter compound, which may be regarded as the condensation product of trihalonitrosomethane and formaldehyde, undergoes thermal decomposition with the formation of the final reaction products.



The decomposition of trihaloacethydroxamic acids to form trihalonitrosomethane and formaldehyde is a new type of rearrangement of hydrosamic acids.

EXPERIMENTAL

Monofluoroacethydroxamic acid. With stirring and cooling in ice, 16.7 g of methyl fluoroacetate was slowly added dropwise to a freshly prepared solution of 5.0 g of hydroxylamine in 100 ml of methanol. A small amount of heat was evolved and the reaction mixture acquired a light yellow color. When the ester had been added, stirring was continued for a further 2 hr and then the solution was evaporated in vacuum at room temperature to $^1/_3$ of its original volume; the solution deposited a white, crystalline precipitate. The precipitate was collected by filtration and the mother liquor evaporated to dryness in vacuum. The residue (6.7 g) was recrystallized twice from dry ethyl acetate to yield white crystals of monofluoroacethydroxamic acid with m. p. 75-76°. The yield was 40%.

Found %: C 25.61; H 4.70; N 15.35; F 20.08. $C_2H_4O_2NF$. Calculated %: C 25.83; H 4.31; N 15.06; F 20.45.

The sodium salt of monofluoroacethydroxamic acid was obtained by precipitation from a cold methanol solution of the acid, which was neutralized with sodium methylate or sodium hydroxide in methanol.

Found %: N 12.32; F 16.14. $C_2H_3O_2NFNa$. Calculated %: N 12.17; F 16.52.

Fluorodichloroacethydroxamic acid. Similarly, from 4.3 g of hydroxylamine and 16.5 g of methyl fluorodichloroacetate we obtained 10.1 g of fluorodichloroacethydroxamic acid with m. p. 94.5-95° (from ethyl acetate). The yield was 61%.

Found %: C 14.64; H 1.45; N 8.89; F 11.42; Cl 43.60. $C_2H_2O_2NFCl_2$. Calculated %: C 14.81; H 1.23; N 8.66; F 11.72; Cl 43.85.

Trichloroacethydroxamic acid. Similarly, from 11.2 g of hydroxylamine and 30.0 g of methyl trichloroacetate we obtained 25.5 g of trichloroacethydroxamic acid with m. p. 78-79° (from a mixture of chloroform and ligroin). The yield was 85%.

Found %: N 8.02; Cl 59.26. $C_2H_2O_2NCl_3$. Calculated %: N 7.85; Cl 59.62.

The sodium salt of trichloroacethydroxamic acid was obtained by precipitation from a cold methanol solution of the acid, which was neutralized with sodium methylate or sodium hydroxide in methanol.

Found %: N 7.14; Cl 52.70; C 12.33. $C_2HO_2NCl_3Na$. Calculated %: N 6.99; Cl 53.06; C 11.98.

The potassium salt of trichloroacethydroxamic acid was obtained analogously.

Found %: N 6.50. $C_2HO_2NCl_3K$. Calculated %: N 6.57.

Trifluoroacethydroxamic acid. Similarly, from 6.4 g of hydroxylamine and 25.0 g of methyl trifluoroacetate we obtained 19.0 g of trifluoroacethydroxamic acid with m.p. 75-76° (from a mixture of chloroform and ligroin), which sublimed when heated to 70° at 15-18 mm. The yield was 76%.

Found %: C 18.86; H 1.78; N 10.64; F 43.91. $C_2H_2O_2NF_3$. Calculated %: C 18.61; H 1.55; N 10.86; F 44.17.

The sodium salt of trifluoroacethydroxamic acid was obtained by precipitation from a cold methanol solution of the acid, which was neutralized with sodium methylate or sodium hydroxide in methanol.

Found %: N 9.45; F 37.40. $C_2HO_2NF_3Na$. Calculated %: N 9.28; F 37.75.

The potassium salt of trifluoroacethydroxamic acid was obtained analogously.

Found %: N 8.52. $C_2HO_2NF_3K$. Calculated %: N 8.38.

Basicity of trifluoroacethydroxamic acid. After various time intervals, to a solution of a sample of trifluoroacethydroxamic acid (0.1-0.2 g) in 50 ml of water was added 20 ml of 0.1 N sodium hydroxide solution and the excess of the latter titrated with 0.1 N hydrochloric acid to thymolphthalein*. The amount of alkali bound, expressed in equivalents per mole of trifluoroacethydroxamic acid, is given in Table 1.

Thermal decomposition of trichloroacethydroxamic acid. Into a flask with an outlet tube connected successively to a receiver cooled with ice and a trap cooled with a mixture of acetone and carbon dioxide was placed 8.9 g of trichloroacethydroxamic acid. The latter was carefully heated to 90-95° at a pressure of 20-30 mm. Vigorous decomposition, accompanied by the evolution of gases and solids, was observed. The gases, which had a blue color, condensed in the trap in the form of a blue liquid. The solid partly sublimed and condensed in the receiver. At the end of the decomposition, the temperature was raised to 140-150° and heating continued for about an hour. A tarry residue (2.1 g) remained in the flask.

TABLE 1

Time, hr	Alkali equivalent		Relative alkali equivalent	
	sample 1	sample 2	sample 1	sample 2
0,17	1,20	1,20	1,38	1,36
10	1,12	1,15	1,29	1,31
24	1,04	1,06	1,20	1,21
48	0,975	0,985	1,12	1,12
96	0,92	0,915	1,06	1,04
144	0,87	0,89	1,00	1,01
240	0,87	0,88	1,00	1,00

The condensate (4.6 g) was fractionated to yield trichloronitrosomethane with b. p. 5-7°/70 mm and d_4^{20} 1.457. The yield was 62%. The molecular weight found was 145.0 and that calculated, 148.4.

* The indicator was chosen arbitrarily as the strength of trifluoroacethydroxamic acid was not determined.

Found %: Cl 71.15. $CONCl_3$. Calculated %: Cl 71.71.

B. p. 5°/70 mm and d 1.506 is reported for trichloronitrosomethane in the literature.

Hydrocyanic acid (test for Prussian blue) and carbon dioxide (test with barium hydroxide solution) were detected in the emergent gases from the distillation of trichloronitrosomethane.

The sublimate (0.9 g) was a white, amorphous substance, which dissolved in water, sublimed readily and completely, and was paraformaldehyde. The yield was 60%.

Found %: 1.01 iodine equivalent. CH_2O. Calculated %: 1.00 iodine equivalent.

Thermal decomposition of trifluoroacethydroxamic acid. Analogously, heating 13.0 g of trifluoroacethydroxamic acid to 80-85° at 30-40 mm gave trifluoronitrosomethane with b. p. −85 to −82°. The yield was 63%. The molecular weight found was 96 and that calculated, 99.

Found %: F 57.1. $CONF_3$. Calculated %: F 57.6.

B.p. − 86° is reported for trifluoronitrosomethane in the literature.

Carbon dioxide was detected in the emergent gases from the distillation of trifluoronitrosomethane; hydrocyanic acid was detected in the residue.

The sublimate (2.2 g) was paraformaldehyde. The yield was 73%.

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HOMOLYTIC ADDITION OF HYDROGEN BROMIDE TO 1-FLUORO-1,1-DICHLOROPROPENE

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The presence of fluorine in polyhalomethyl groupings makes the C—Hal bond in them more inert to heterolytic and also homolytic scission. In particular, fluorine has a substantial effect on the capacity of compounds with the structure $\diagdown C = C - CX_3$ (where X = Cl or F) to undergo anionotropic allyl rearrangement, sometimes making the reaction proceed in a direction opposite to that observed in polychloro derivatives. An example is the formation of $CHCl = CCl - CF_3$ (1) from $CHCl_2CCl = CCl_2$ (2) [1] during the reaction of the latter with antimony trifluoride, while with polychloro derivatives, the isomerization of substances of type (1) into substances of type (2) is usually observed. In [2 and 3] we studied the allyl rearrangement of a number of polyhalopropenes with the structure $CH_2 = CRCX_3$, where R = H or Cl and $CX_3 = CCl_3$, CCl_2F, $CClF_2$. It was shown that the capacity for allyl rearrangement falls sharply with successive replacements of chlorine in the trichloromethyl group of polychloropropenes by fluorine [3].

In the present work we also demonstrated a definite difference in the behavior of 1-fluoro-1,1-dichloropropene in a homolytic addition reaction in comparison with 1,1,1-trichloropropene. The reaction of 1-fluoro-1,1-dichloropropene with hydrogen bromide with irradiation with ultraviolet light yielded two fluorodichlorobromopropanes, 1-fluoro-1,1-dichloro-3-bromopropane, and 1-fluoro-1,2-dichloro-3-bromopropane in a ratio of 2:1. The reaction proceeded by a free radical chain mechanism, as indicated by the conditions under which the reaction was carried out (the need for irradiation with ultraviolet light) and also inhibition of the addition by small amounts of hydroquinone or acetone. The addition of hydrogen bromide to 1,1,1-trichloropropene under these conditions leads to a single addition product, 1,1,2-trichloro-3-bromopropane, i.e., its proceeds with rearrangement of the intermediate free radical similar to that described previously [4] for the reaction initiated by benzoyl peroxide.

The reaction of fluorodichloropropene with hydrogen bromide may be illustrated by scheme 1:

$$CH_2 = CHCCl_2F + Br \rightarrow CH_2BrC\dot{H}CCl_2F$$

$$\begin{array}{ll} CH_2BrC\dot{H}CCl_2F & \rightarrow CH_2BrCHCl\dot{C}ClF \\ \downarrow HBr & \downarrow HBr \\ CH_2BrCH_2CCl_2F + Br & CH_2BrCHClCClFH + Br \end{array} \qquad (I)$$

Thus, apparently as a result of the stabilizing action of fluroine in the radical $CH_2BrC\dot{H}CCl_2F$, the rate of rearrangement of the latter is considerably reduced and becomes commensurate with the rate of its reaction with hydrogen bromide. It should be noted that such a double reaction of a free radical (with rearrangement and without it) in the polyhaloalkyl series was observed for the first time (cf. [4-9]).

The structures of the fluorodichlorobromopropanes were demonstrated in the following way. Firstly, these compounds were synthesized by a known route according to schemes II and III:

$$CCl_3CH_2CH_2Br + SbF_3 \xrightarrow{SbCl_5} CCl_2FCH_2CH_2Br, \quad \text{(II)}$$

$$CHCl_2CHClCH_2Br + SbF_3 \xrightarrow{SbCl_5} CHClFCHClCH_2Br. \quad \text{(III)}$$

The yield of the fluoride in reaction III was very low. The corresponding fluorodichlorobromopropanes obtained both by scheme I and by schemes II and III were identified in the form of crystalline picrates of their isothiuronium derivatives. In addition, dehydrobromination of 1-fluoro-1,1-dichloro-3-bromopropane yielded the starting 1-fluoro-1,1-dichloropropene. Dehydrobromination of 1-fluoro-1,2-dichloro-3-bromopropane yielded 1-fluoro-1,2-dichloro-2-propene, whose structure was demonstrated by ozonization, which yielded (after hydrolysis of the ozonide) formaldehyde and fluorochloroacetic acid. The starting 1-fluoro-1,1-dichloropropene was synthesized in two stages from 1,1,1,3-tetrachloropropane by somewhat modified methods [3].

EXPERIMENTAL

Synthesis of 1-fluoro-1,1,3-trichloropropane and 1-fluoro-1,1-dichloropropene. 1-Fluoro-1,1,3-trichloropropane was prepared as described in [3]. So that mainly monofluoride would be formed, the ratio of the reagents was changed. We used 0.5 mole of antimony trifluoride and 3 ml of antimony pentachloride to 1 mole of 1,1,1,3-tetrachloropropane. The yield of 1-fluoro-1,1,3-trichloropropane was 45% of theoretical.

1-Fluoro-1,1,3-trichloropropane was dehydrochlorinated by the procedure described in [3], but in an ethyl cellosolve medium. As a result, in addition to 1-fluoro-1,1-dichloropropene, which was obtained in 59% yield, we were able to isolate 1-fluoro-1,3-dichloro-1-propene in a yield of 10% of theoretical and this had b. p. 89-90° n_D^{20} 1.4350; d_4^{20} 1.3219. Literature data [3]: b. p. 88.5-89.5°, n_D^{20} 1.4310; d_4^{20} 1.3186. The picrate of the isothiuronium derivative had m. p. 176-177° (from aqueous alcohol).

Found %: N 17.31; 17.51. $C_{10}H_9FClN_5O_7S$. Calculated %: N 17.30.

Addition of hydrogen bromide to 1-fluoro-1,1-dichloropropene. A stream of hydrogen bromide was passed for 10 hr through 50 g of fluorodichloropropene in a quartz tube, illuminated with a PRK-4 lamp. The reaction product was washed with soda and water and dried over calcium chloride. Distillation yielded two addition products.

The first product was 1-fluoro-1,1-dichloro-3-bromopropane (32 g) with b. p. 69-70°/70 mm; 136°/760 mm; n_D^{20} 1.4630; d_4^{20} 1.7307; MR: found, 33.43; calculated 33.45.

Found %: C 17.29, 17.16; H 1.94, 1.93; F 9.76, 9.81. $C_3H_4FCl_2Br$. Calculated %: C 17.16; H 1.92; F 9.05.

The picrate of the isothiuronium derivative had m. p. 164° (from alcohol).

Found %: C 27.36, 27.35; H 2.28, 2.24; N 16.06. $C_{10}H_{10}FCl_2N_5O_7S$. Calculated %: C 27.66; H 2.32; N 16.13.

Dehydrobromination of this fluorodichlorobromopropane with alkali in ethyl cellosolve at 0° gave a 60% yield of the starting 1-fluoro-1,1-dichloropropene. 1-Fluoro-1,1-dichloro-3-bromopropane synthesized by a known route by the reaction of 1,1,1-trichloro-3-bromopropane with antimony trifluoride* had b. p. 136°; n_D^{20} 1.4630; d_4^{20} 1.7295. The picrate of its isothiuronium derivative melted at 164°. A mixed melting point of the two picrates was not depressed.

The second product was 1-fluoro-1,2-dichloro-3-bromopropane (15 g) with b. p. 72-73°/40 mm; 161°/760 mm; n_D^{20} 1.4870; d_4^{20} 1.8200; MR: found, 33.17, calculated 33.45.

Found %: C 17.18, 17.04; H 1.87, 1.82; F 8.99, 9.20. $C_3H_4FCl_2Br$. Calculated %: C 17.16; H 1.92; F 9.05.

The picrate of the isothiuronium derivative had m. p. 171° (from alcohol).

Found %: C 27.34, 27.39; H 2.29, 2.19; N 15.98. $C_{10}H_{10}FCl_2N_5O_7S$. Calculated %: C 27.66; H 2.32; N 16.13.

*1,1,3-Trichloro-1-propene was also formed during the fluorination. For isolation of 1-fluoro-1,1-dichloro-3-bromopropane, the mixture was treated with bromine and then the products were readily separated by fractionation.

Dehydrobromination of this fluorodichlorobromopropane with alkali in ethyl cellosolve at 0° gave a 54% yield of 1-fluoro-1,2-dichloro-2-propene with b. p. 84°; n_D^{20} 1.4290; d_4^{20} 1.3214: MR: Found 25.10, calculated 25.22.

Found %: C 28.31, 28.25; H 2.42, 2.50. $C_3H_3FCl_2$. Calculated %: C 27.93; H 2.34.

The picrate of the isothiuronium derivative had m. p. 160-161° (darkened at 149°).

Found %: C 29.86, 29.95; H 2.49, 2.47; F 4.57, 4.56. $C_{10}H_9FClN_5O_7S$. Calculated %: C 30.19; H 2.28; F 4.77.

When this fluorodichloropropene was ozonized and the ozonide then decomposed with water we isolated formaldehyde as its dimedone derivative with m. p. 189° (literature data [10]: m. p. 189°), and fluorochloroacetic acid with b. p. 162°, n_D^{20} 1.4090, (literature data [11]: b. p. 162° n_D^{25} 1.4085), which was converted through the acid chloride into the anilide of the acid with m. p. 86-87° (from heptane).

Found %: C 51.31, 51.32; H 3.89, 3.87; F 10.18, 10.17. C_8H_7FClNO. Calculated %: C 51.22; H 3.76; F 10.13.

A mixed melting point with the anilide obtained from authentic fluorochloroacetic acid was not depressed. 1-Fluoro-1,2-dichloro-3-bromopropane was also obtained, though in very low yield, by a known route by the reaction of 1,1,2-trichloro-3-bromopropane with antimony trifluoride and had b. p. 161-162°; n_D^{20} 1.4860; d_4^{20} 1.8194. The picrate of its isothiuronium derivative melted at 169°. A mixed melting point of the two picrates was not depressed.

Addition of hydrogen bromide to 1,1,1-trichloropropene. The experiment was carried out as in the case of 1-fluoro-1,1-dichloro-2-propene. Saturation of 50 g of trichloropropene with hydrogen bromide for 2.5 hr and appropriate treatment and distillation yielded 68 g of 3-bromo-1,1,2-trichloropropane with b. p. 84-85°/16 mm; n_D^{20} 1.5295; d_4^{20} 1.8390. Literature data [4]: b. p. 75-75.5°/9 mm; n_D^{20} 1.5290; d_4^{20} 1.8322.

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INVESTIGATION OF THE MECHANISM OF THE ANTHRANILIC REARRANGEMENT BY MEANS OF O^{18}

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The action of aqueous alkali on o-nitrotoluene yields a series of products of which the most important is anthranilic acid [1]. The mechanism of this reaction, which is called the anthranilic rearrangement, is of importance in understanding oxidation, reduction, isomerization, and condensation reactions of aromatic nitro compounds. It has been investigated by a number of authors, but none of the reaction schemes proposed up to now could be unequivocally confirmed or refuted on the basis of available literature data.

The present work was planned to solve a problem which is important for understanding the rearrangement mechanism, namely, whether the oxygen of the carboxyl group of the anthranilic acid arises from the nitro group of the original o-nitrotoluene or from the aqueous alkali. For this purpose we investigated the conversion of o-nitrotoluene into anthranilic acid and of the potassium salt of o-nitrotoluene-p-sulfonic acid into p-sulfoanthranilic acid by the action of aqueous KOH labeled with O^{18}. The reaction mechanism was determined from the O^{18} contents of the anthranilic and p-sulfoanthranilic acids formed.

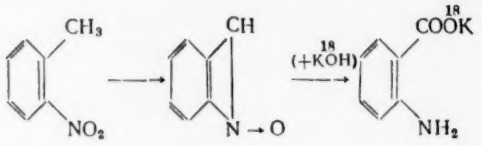
The results of typical experiments are given below.

To 0.24 mole of o-nitrotoluene, heated to 200° in a flask with a reflux condenser, was added a solution of 0.45 mole of $KO^{18}H$ in 0.90 mole of H_2O^{18}. The temperature of the reaction mixture fell to 150° over a period of 15 min. This temperature was maintained until the end of the reaction. The reaction mixture was then steam distilled to remove unreacted o-nitrotoluene and o-toluidine and the residue neutralized with dilute H_2SO_4. A stream of CO_2 was passed through the liquid to remove hydrocyanic acid and the mixture filtered; the filtrate was acidified with acetic acid and copper acetate added to precipitate copper anthranilate The latter was treated with hydrogen sulfide and the anthranilic acid formed extracted with ether and then sublimed after removal of the ether. The m. p. was 148°. In various experiments, we varied the time for adding the alkali from 20 to 90 min and the duration of the subsequent heating of the reaction mixture from 15 to 120 min. The excess O^{18} content of the anthranilic acid isolated varied insignificantly and was 41-48% of the excess O^{18} content of the original aqueous alkali (0.60 at. %).

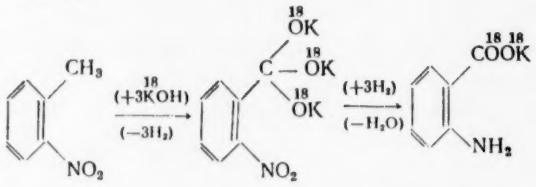
Over a period of 15 to 60 min, 0.04 mole of potassium o-nitrotoluene-p-sulfonate was added to a solution of 0.16 mole of $KO^{18}H$ in 1.40 mole of H_2O^{18}, heated in a flask with a reflux condenser on a boiling water bath, and the reaction mixture heated at 100° for a further 60-150 min. The reaction mixture was then neutralized with dilute hydrochloric acid and treated with copper sulfate to precipitate (over a period of a day) copper p-sulfoanthranilate. Decomposition of the latter with hydrochloric acid gave p-sulfoanthranilic acid, whose purity was checked by titration of one sample with alkali and another with sodium nitrite. The excess O^{18} content of the p-sulfoanthranilic acid was 44-48% of the excess O^{18} content of the original aqueous alkali, which was from 0.80 to 2.00 at. % in different experiments.

The data obtained show that in the carboxyl group of the anthranilic and p-sulfoanthranilic acids, one oxygen atom arose from o-nitrotoluene and the second from the aqueous alkali. This observation agrees with the

reaction mechanisms proposed by Scholl [2], Shchukina, and Predvoditeleva [3], and one of the variants of the scheme of Porai-Koshits [4]. All these authors proposed that the anthranilic rearrangement proceeds with the intermediate formation of anthranil.



Our data refute the scheme of Lock [1]:

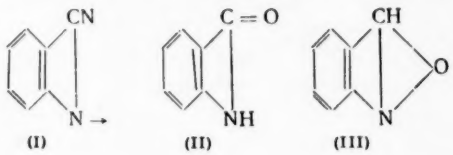


and one of the variants of the scheme of Porai-Koshits in which the formation of the ortho form of the acid was envisaged and also the mechanism of intramolecular oxidation of the methyl group by oxygen of the nitro group, which has been proposed occasionally [5].

In order to confirm the mechanism of type (1), we studied the hydrolysis of anthranil to anthranilic acid by aqueous alkali labeled with heavy oxygen. It was found that the acid contained 40-46% of the amount of excess O^{18} which was present in the aqueous alkali and this was a further argument in favor of a rearrangement mechanism of type (1).

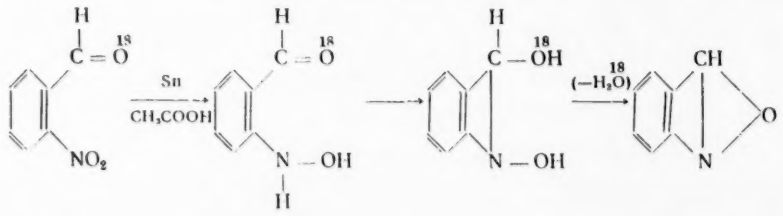
Test experiments showed that isotopic exchange of anthranilic and p-sulfoanthranilic acids during the reaction did not appreciably alter their isotopic composition. There was no isotopic exchange at all of anthranil with H_2O^{18} at 100°.

In addition to investigating the mechanism of the anthranilic rearrangement, we studied the structure of anthranil, for which a series of formulas have been proposed and of these the following three are the most probable:



Up to now it has not been possible to make a conclusive choice between them. We found that anthranil does not exchange its hydrogen with heavy water even after 3 hr at 100°, which unequivocally eliminates the amide formula (II) of Friedlander and Heller [6] as the hydrogen in the N–H grouping exchanges very rapidly.

On reduction of o-nitrobenzaldehyde, labeled with O^{18} in the carbonyl group, it was found that the anthranil formed did not contain excess O^{18} and consequently its oxygen was derived from the nitro group and not from the carbonyl group of the o-nitrobenzaldehyde, which corresponds to the scheme:



These data refute the hypothesis that the carbonyl oxygen is retained in anthranil, which was proposed by Bamberger [7], but not structure (III) that he put forward. We consider that the properties of anthranil correspond best to formula (I), which was proposed in [8] and was supported by recent work [3].

The results of our experiments with o-nitrobenzaldehyde show, on the other hand, that, as has sometimes been proposed [4], this substance may be an intermediate product in the anthranilic rearrangement, preceding anthranil, as according to our data the oxygen of the nitro group, which does not exchange with aqueous alkali, passes into the anthranil. The O^{18} content of the water and organic substances was determined with a mass spectrometer by the method developed in our laboratory [9, 10]. The accuracy of the analyses was 3%.

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THE ARBUZOV REARRANGEMENT OF VINYL ESTERS OF PHOSPHOROUS AND PHENYLPHOSPHINOUS ACIDS

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We recently described a method of synthesizing previously inaccessible vinyl esters of phosphorous acid [1] of the type $(RO)_2POCH = CH_2$, $ROP(OCH = CH_2)_2$ and $P(OCH = CH_2)_3$ and also some reactions of these compounds. In the present article we present the results of studying the Arbuzov rearrangement of vinyl esters of phosphorous and phenylphosphinous acids. As might have been expected, the isomerization of vinyl esters of phosphorous acid to vinyl esters of phosphinic acids proceeded with greater difficulty than the isomerization of trialkyl phosphites. Thus, while heating with methyl iodide on a water bath for 2 hr was sufficient for quantitative isomerization of triethyl phosphite into diethyl methylphosphinate [2], the rearrangement of diethyl vinyl phosphite to ethyl vinyl methylphosphinate required heating with methyl iodide for 4 hr. The isomerization of the various dialkyl vinyl phosphites we prepared required heating with methyl iodide for 4-6 hr. When dialkyl vinyl phosphites were heated at 100° with ethyl iodide and butyl iodide, less than 50% isomerization occurred in 20 hr and hence the reaction had to be carried out in sealed tubes at 120-150° for 8 hr. Under these conditions we obtained a series of alkyl vinyl esters of phosphinic acids, whose constants are given in Table 1.

Alkyl divinyl phosphites were isomerized to divinyl esters of alkylphosphinic acids under even more drastic conditions. Only 60% isomerization occurred when a mixture of ethyl divinyl phosphite and methyl iodide was heated on a boiling water bath for 20 hr. Heating the same system in a sealed tube (110°, 8 hr) gave divinyl methylphosphinate in 88% yield.

Divinyl esters of ethyl-, propyl-, and butylphosphinic acids were prepared by heating alkyl divinyl phosphites with the alkyl iodide containing the same radical as the phosphite in sealed tubes (130-160°, 8 hr). The isomerization of alkyl divinyl phosphites with an alkyl halide containing a radical differing from the alkyl radical of the phosphite gave a mixture of phosphinic esters. Trivinyl phosphite was not isomerized by prolonged heating with methyl iodide. Carrying out the isomerization in a sealed tube at 120-125° led to resinification of the reaction products.

Thus, in the case of monovinyl and divinyl phosphites, the Arbuzov rearrangement proceeded with elimination of an alkyl radical. The elimination of a vinyl radical was not observed in any of the cases.

On the basis of the results obtained for the isomerization of vinyl phosphites to vinyl phosphinates, it might have been expected that the Arbuzov rearrangement of divinyl phenylphosphinite would also be difficult. Divinyl phenylphosphinite, which was obtained from phenyldichlorophosphine and mercuribisacetaldehyde, reacted with methyl iodide to give a crystalline addition product. When this compound was heated, iodine was liberated and resinification occurred.

We also studied the reaction of vinyl phosphites with acyl halides (acetyl and benzoyl chlorides). There was slight heat evolution when dialkyl vinyl phosphites were mixed with acyl halides. The reaction occurred at

TABLE 1

Vinyl Esters of Phosphinic Acids

Compound	Isomerization conditions: hr.	°C	Yield, %	B. p., °C/mm	n_D^{20}	d_4^{20}	MRD: found	MRD: calc.	Found %: C	Found %: H	Found %: P	Calculated %: C	Calculated %: H	Calculated %: P
$CH_2P(O)(OC_2H_3)OR$*	4	100	80	82—83/25	1.4265	1.0775	35.74	35.69	39.75	7.62	19.92	40.00	7.30	20.63
$CH_2P(O)(OC_2H_3)OR$	6	100	90	79—7 .5/8	1.4290	1.0447	40.51	40.33	43.87	8.00	18.72	43.90	7.90	18.87
$CH_2P(O)(OC_2H_3)OR$	6	100	86	79.5—80/3.5	1.4320	1.0232	45.16	44.92	47.16	8.64	17.07	47.30	8.10	17.39
$CH_2P(O)(OC_2H_3)OR$	8	120	60	93—96/1.5	1.4335	1.0070	49.51	49.54	49.90	9.07	15.84	49.59	8.92	16.15
$C_2H_5P(O)(OC_2H_3)OR$	8	150	85	83.5—84/1	1.4369	0.9786	58.95	58.97	54.48	9.52	14.01	54.53	9.01	14.02
$C_2H_5P(O)(OC_2H_3)OR$	8	120	80	69—69.5/6	1.4291	1.0485	40.36	40.31	43.80	8.06	18.32	43.90	7.98	18.87
$C_2H_5P(O)(OC_2H_3)OR$	8	110	86	62.5—63/6.5	1.4388	1.1130	35.31	35.25	40.77	6.42	20.62	40.55	6.13	20.92
$CH_2P(O)(OR)_2$	8	130	82	66—67/1	1.4393	1.0714	39.57	39.54	44.62	7.08	18.94	44.45	6.83	19.11
$C_2H_5P(O)(OR)_2$	8	140	65	71—71.5/3.5	1.4403	1.0435	44.56	44.46	47.59	7.69	17.46	47.73	7.44	17.59
$C_2H_5P(O)(OR)_2$	8	160	74	71—72/2	1.4430	1.0224	49.30	49.07	50.64	8.19	16.00	50.52	7.95	16.29
$C_2H_5P(O)(OC(CH_3)=CH_2)_2$	8	130	82	63.5—70/2	1.4470	1.0392	48.90	49.07	50.59	8.10	16.11	50.52	7.95	16.29
$CH_3COP(O)(OC_2H_3)OR$	48	20	63	76,5/2	1.4332	1.1310	41.11	40.32	40.55	6.45	17.17	40.45	6.23	17.32
$CH_3COP(O)(OC_2H_3)OR$	48	20	58	67—68/1	1.4361	1.0940	45.91	44.85	43.84	6.93	15.84	43.76	6.82	16.13
$CH_3COP(O)(OC_2H_3)OR$	48	20	70	91—92/1	1.4390	1.0739	50.50	49.54	46.26	7.68	14.45	46.69	7.33	15.03
$C_2H_5COP(O)(OC_2H_3)OR$	48	20	83	147—148/3	1.5168	1.1453	66.97	64.43	56.79	8.01	12.14	56.68	8.04	12.16
$C_6H_5COP(O)(OR)_2$	8	120	50	135—137/1	1.5315	1.1961	61.65	59.32	55.21	5.05	12.78	55.47	4.65	13.01

* $R = (CH_2 = CH-)$.

room temperature over a period of 2 days. Distillation of the reaction products yielded vinyl esters of α-keto-phosphinic acids, whose constants and yields are given in Table 1.

The reaction of alkyl divinyl phosphites with acyl halides required more drastic conditions, as was found for the reaction of benzoyl chloride with butyl divinyl phosphite.

EXPERIMENTAL

Ethyl vinyl methylphosphinate. To 7.7 g (0.054 mole) of methyl iodide was added 8.2 g (0.05 mole) of diethyl vinyl phosphite. The mixture was heated on a boiling water bath for 4 hr. Distillation yielded 5 g of ethyl iodide (65%) and 6.7 g (89% of theoretical) of ethyl vinyl methylphosphinate.

Butyl vinyl butylphosphinate. To 10 g (0.054 mole) of butyl iodide was added 10.6 g (0.05 mole) of dibutyl vinyl phosphite. The mixture was heated in a sealed tube at 150° for 8 hr. Distillation yielded 8 g of butyl iodide (80%) and 9.3 g (85% of theoretical) of butyl vinyl butylphosphinate.

Divinyl methylphosphinate. To 12 g (0.08 mole) of methyl iodide was added 10 g (0.06 mole) of ethyl divinyl phosphite. The mixture was heated in a sealed tube at 110° for 8 hr. Distillation under reduced pressure yielded 8 g (88% of theoretical) of divinyl methylphosphinate.

Diisopropenyl ethylphosphinate. To 10 g (0.06 mole) of ethyl iodide was added 10 g (0.056 mole) of ethyl diisopropenyl phosphite. The mixture was heated in a sealed tube at 130° for 8 hr. Distillation yielded 6 g (60%) of ethyl iodide and 8.8 g (82% of theoretical) of diisopropenyl ethylphosphinate.

Ethyl vinyl acetylphosphinate. To 4.8 g (0.06 mole) of acetyl chloride was added 10 g (0.06 mole) of diethyl vinyl phosphite. The mixture was left at room temperature for 48 hr. Distillation yielded 6.8 g (63% of theoretical) of ethyl vinyl acetylphosphinate.

Divinyl benzoylphosphinate. To 6.5 g (0.05 mole) of benzoyl chloride was added 9.3 g (0.05 mole) of butyl divinyl phosphite. The mixture was heated at 115-120° for 8 hr. Distillation yielded 5.9 g (50% of theoretical) of divinyl benzoylphosphinate.

Divinyl phenylphosphinite. With vigorous stirring in a stream of nitrogen, a solution of 35.8 g (0.2 mole) of phenyldichlorophosphine in 50 ml of isopentane was added dropwise to 60 g (0.2 mole) of mercuribisacetaldehyde and 20.2 g (0.2 mole) of triethylamine in 300 ml

of isopentane. When half of the phenyldichlorophosphine solution had been added, a further 60 g (0.2 mole) of mercuribisacetaldehyde and 20.2 g (0.2 mole) of triethylamine were introduced into the reaction mixture and then the second half of the phenyldichlorophosphine solution added dropwise. The reaction mixture was then stirred for a further 1.5 hr. After the precipitate had been removed and the isopentane evaporated, the residue was vacuum distilled. We obtained 17 g (43% of theoretical) of divinyl phenylphosphinite with b. p. 76-78°/2 mm; n_D^{20} 1.5385, d_4^{20} 1.0633. MR_D found 57.16, calculated 57.37.

Found %: C 61.54, 61.20; H 6.10, 5.85; P 15.25, 15.13. $C_{10}H_{11}O_2P$. Calculated %: C 61.85; H 5.71; P 15.95.

Addition product of methyl iodide and divinyl phenylphosphinite. To a solution of 1.6 g of methyl iodide in 3 ml of acetone was added 2 g of divinyl phenylphosphinite and the mixture left overnight. During this time an oil precipitated and this crystallized on cooling. The crystals were collected and washed with cool acetone. We obtained 2 g (58% of theoretical) of product with m p. 37-38°.

Found %: C 38.89, 38.56; H 4.32, 4.26; P 9.19, 9.07. $C_{11}H_{14}O_2P$. Calculated %: C 39.31; H 4.20; P 9.21.

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SOME DERIVATIVES OF 1-THIONAPHTHEN-3-ONE-1-DIOXIDE

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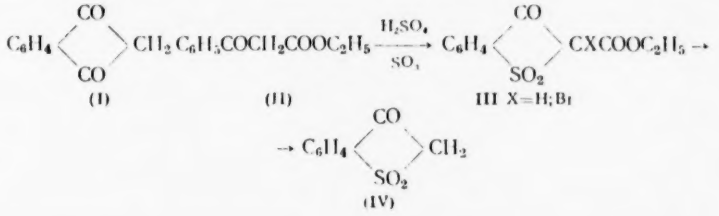
Many derivatives of 1,3-indandione (I) have found practical application as analytical reagents (2-nitro-1,3-indandione, ninhydrin, bindin, 2-nitroso-1,3-indandione, etc.), and as blood anticoagulants and dodenticides* (2-phenyl-1,3-indandione, 2-diphenylacetyl-1,3-indandione, 2-pivalyl-1,3-indandione, etc.), and have been proposed as narcotics, analytical reagents, and spasmolytics (many 2-amino-2-arylindandiones) [1-9]. Therefore, it seemed interesting to study derivatives of analogs of 1,3-indandione. We first studied 1-thionaphthen-3-one-1-dioxide (IV), in which one of the CO groups has been replaced by an SO_2 group; the latter is often encountered in physiologically active substances.

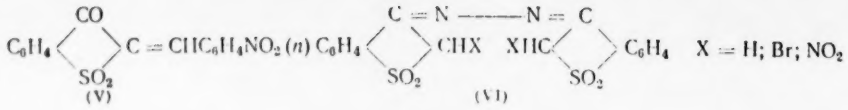
1-Thionaphthen-3-one-1-dioxide is obtained by oxidation of thioindoxyl with hydrogen peroxide [10]. By sulfonating the benzoylacetic ester (II), Feist [11] prepared the ester of the anhydrobenzoyl-o-sulfonic acid (III) and obtained as a by-product 1-thionaphthen-3-one-1-dioxide (IV), which was evidently formed by hydrolysis of the above ester. Arndt et al., [12] heated the ester for 8 hr with 20% hydrochloric acid and recovered the original ester; the same result was obtained when the ester was boiled for 5 hr in the presence of sulfuric acid in methanol. We carried out the hydrolysis with 20% sulfuric acid in ethanol and obtained (IV) in 83.8% yield.



Ester (III) (X = H) had acid properties and readily formed salts; the potassium, ammonium, aniline, and piperidine salts were prepared. An alcohol solution of the ester gave a red color with $FeCl_3$. Like esters of indandionecarboxylic acid, the ester was readily brominated; when brominated under mild conditions it formed III (X = Br) and when brominated more vigorously it formed 2,2-dibromo-1-thionaphthen-3-one-1-dioxide.

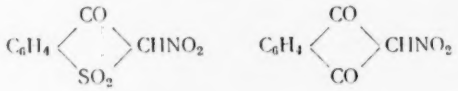
1-Thionaphthen-3-one-1-dioxide (IV) formed colorless crystals with m. p. 134-135° (m. p. of 1,3-indandione 129-131°). It dissolved in alkalis to form a colorless solution (indandione gives a yellow one) and was liberated unchanged on acidification. It did not dissolve in cold water and when an aqueous solution was boiled it became pink and gave an acid reaction. In contrast to the original ester, it did not give a red color with $FeCl_3$ in alcohol [11]. The presence of an active methylene group in IV was demonstrated by the preparation of a condensation product (V) with p-nitrobenzaldehyde. Bromination of IV yielded both a monobromo and a dibromo derivative. The phenylhydrazone and oxime were prepared. Their properties corresponded to literature data [13, 14]. The methyl ether and the benzoate were prepared from the oxime.

*As in Russian original.



(V) (VI)

The reaction of IV with $NH_2NH_2 \cdot HCl$ yielded the azine (VI) in the form of yellow crystals. Its methylene group remained untouched and therefore the azine was readily brominated (VI, X = Br) and nitrated (VI, X = NO_2). On hydrolysis of the latter compound, one would expect to obtain 2-nitro-1-thionaphthen-3-one-1-dioxide (VII), but it could be prepared more simply, namely by direct nitration of IV similar to the preparation of 2-nitro-1,3-indandione (VIII). Compound VII, which is an analog of VIII, is a very interesting substance; a study and comparison of the properties of VII and VIII may give much information for solving a number of theoretical problems. A special communication on compound VII will follow.



(VII) (VIII)

EXPERIMENTAL

Ethyl ester of 1-thionaphthen-3-one-1-dioxide-2-carboxylic acid (or anhydrobenzoyl-o-sulfonic acid) (III, X = H). Over a period of half an hour, 40 g of ethyl benzoylacetate was added from a dropping funnel with vigorous stirring to 200 g of 60% oleum, cooled with ice and salt. The sirupy reaction product was poured onto five times the amount of ice. The white crystalline precipitate of III (X = H) obtained was repeatedly recrystallized from alcohol. The yield was 38 g (82%). The m. p. was 140°. According to literature data the yield is 60% [12] and the m. p. 140°.

Potassium salt. An alcohol solution of III (X = H) was neutralized with a saturated aqueous solution of K_2CO_3. On standing, the filtrate deposited colorless, rhombic platelets of the potassium salt. The m. p. was 312° (decomp.).

Found %: C 45.20; H 3.66; K 12.92. $C_{11}H_9O_5SK$. Calculated %: C 45.20; H 3.08; K 13.36.

Ammonium salt. An alcohol solution of III (X = H) was saturated with ammonia and left till next day. Fine colorless crystals were formed. The m. p. was 214° (decomp.).

Found %: N 5.02. $C_{11}H_9O_5SNH_4$. Calculated %: N 5.17.

Aniline salt. To an alcohol solution of III (X = H) was added an ether solution of aniline to precipitate colorless needles. The m. p. was 198°.

Found %: N 4.43. $C_{17}H_{14}O_5SN$. Calculated %: N 4.03.

Piperidine salt. This was prepared analogously to the previous salt. It formed colorless platelets with m. p. 161-163° (decomp.).

Found %: N 4.44. $C_{16}H_{21}O_5SN$. Calculated %: N 4.13.

All these salts crystallized readily from alcohol or from alcohol with ether added

Bromination. To 0.3 g of III (X = H) in 10 ml of chloroform was added 10 drops of bromine and the mixture left for several hours in the sun. The chloroform was evaporated and the residue recrystallized from dry CCl_4. The colorless crystals of III (X = Br) had m. p. 99-100°; m. p. 98.5° is reported in the literature [11]. The compound was readily soluble in acetone and $CHCl_3$, difficultly so in CCl_4, and insoluble in water.

Found %: Br 24.36. $C_{11}H_9O_5SN$. Calculated %: Br 24.02.

More vigorous bromination formed 2,2-dibromo-1-thionaphthen-3-one-1-dioxide (see below).

1-Thionaphthen-3-one-1-dioxide (IV). Five g of III (X= H) was dissolved in an alcohol solution of sulfuric acid. The solution was boiled on a water bath until the evolution of CO_2 ceased (~6 hr). The next day the

colorless needlelike crystals of IV were collected and washed carefully with water. The yield was 3 g (83.8%) and the m. p. 134-135° (132-139° according to literature data [10-12]). The product obtained was sufficiently pure for further treatment. Dilution of the acid alcohol filtrate with twice the volume of water yielded a further small amount of IV as oily crystals. They were dissolved in 5% alkali and precipitated with dilute hydrochloric acid. The m. p. was 134° (from alcohol).

Oxime. A mixture of 0.5 g of IV, 0.5 g of $NH_2OH \cdot HCl$, 1.2 g of anhydrous sodium acetate, and 12 ml of glacial acetic acid was boiled for 3 hr and poured into water when cool. The white precipitate of oxime was recrystallized from dilute acetic acid. The m. p. was 245° (245° according to the literature [14]). The substance dissolved in dilute alkali to form a colorless solution and was liberated unchanged on acidification.

Found %: N 6.89. $C_8H_7O_3SN$. Calculated %: N 7.11.

Methyl ether of the oxime. A few drops of dimethyl sulfate was added to a solution of 0.1 g of the oxime obtained in 5% sodium carbonate and the mixture heated to 90°. Fine white needles precipitated. The m. p. was 148-149° (from dilute alcohol).

Found %: N 6.50. $C_9H_9O_3SN$. Calculated %: N 6.64.

Oxime benzoate. Benzoyl chloride was added dropwise with vigorous shaking to 0.1 g of oxime in 5 ml of 2% sodium hydroxide. A white crystalline precipitate of the benzoate formed. It was washed first with cold water then hot water and recrystallized from glacial acetic acid. The m. p. was 245-246° and a mixture with the original oxime melted at 225°. The product was insoluble in water and ether and difficultly soluble in alcohol.

Found %: N 4.68. $C_{15}H_{11}O_4SN$. Calculated %: N 4.50.

2-p-Nitrobenzal-1-thionaphthen-3-one-1-dioxide (V). Over a period of 1.5 hr, 0.5 g of IV was fused with an equivalent amount of p-nitrobenzaldehyde on an oil bath at 160°. The cooled mass was ground, washed with hot benzene, and recrystallized from nitrobenzene. The yield was 0.3 g of yellow crystals of (V). The product was insoluble in the usual organic solvents. It dissolved in concentrated sulfuric acid, giving an orange color. The m. p. was 285-286°.

Found %: N 4.59. $C_{15}H_9O_5SN$. Calculated %: N 4.44.

Bromination of 1-thionaphthen-3-one-1-dioxide. Bromine was added dropwise to a hot solution of 0.5 g of IV in 20 ml of glacial acetic acid until it was no longer decolorized. The yellow solution obtained was diluted with three times its volume of water and the white, flocculent precipitate recrystallized from alcohol. The white, needlelike crystals of 2-bromo-1-thionaphthen-3-one-1-dioxide melted at 118-120°. The product dissolved readily in chloroform, ether, acetone, benzene, and glacial acetic acid.

Found %: Br 29.95. $C_8H_5O_3Br$. Calculated %: Br 30.65.

The alcohol solution was diluted with water and the precipitate recrystallized from dilute alcohol. The white crystals of 2,2-dibromo-1-thionaphthen-3-one-1-dioxide, which had m. p. 146-147°, dissolved readily in alcohol, chloroform, benzene, and acetone, and with difficulty in ether.

Found %: Br 46.75. $C_8H_{14}O_3SBr_2$. Calculated %: Br 47.06.

The same dibromide was obtained by vigorous treatment of ester III (X = H) with bromine. To 0.7 g of (III) (X = H) in 20 ml of glacial acetic acid was added 20 drops of bromine and the mixture boiled for 2 hr. HBr was liberated. The cooled solution was poured into water and the white precipitate recrystallized from dilute alcohol. The m. p. was 146-147°, which was not depressed by admixture with the above dibromide.

Azine of 1-thionaphthen-3-one-1-dioxide VI (X = H). To a solution of 0.2 g of IV in 10 ml of alcohol was added 0.2 g of $N_2H_4 \cdot HCl$ and the mixture boiled for half an hour; fine yellow crystals of VI (X = H) precipitated and these were washed with hot water. The m. p. was 148-149° (decomp.) (from nitrobenzene).

Found %: N 7.48. $C_{16}H_{12}O_4S_2N_2$. Calculated %: N 7.77.

The product was insoluble in the usual organic solvents. On heating, it dissolved in 5% potassium hydroxide to give a brighter color, which disappeared on acidification. The substance dissolved in concentrated sulfuric acid without coloration and dilution with water produced a white turbidity.

Bromination. To a suspension of 0.3 g of VI (X = H) in 10 ml of glacial acetic acid was added 10 drops of bromine and the mixture boiled until the precipitate dissolved. After a few minutes, an orange precipitate of VI (X = Br) formed. It was recrystallized from glacial acetic acid. The m. p. was 240° (vigorous decomp.). The product was insoluble in the usual organic solvents and difficultly soluble in glacial acetic acid and ethylene bromide.

Found %: N 4.11. $C_{16}H_8O_4S_2N_2$. Calculated %: N 4.14.

Nitration. To a suspension of VI (X = H) in glacial acetic acid was added a few drops of fuming nitric acid (d 1.5) and the mixture heated to boiling; the azine gradually dissolved. Bright yellow crystals of VI (X = NO_2) precipitated when the solution was cooled. The m. p. was 168° (with deflagration).

Found %: N 12.34. $C_{16}H_{10}O_8S_2N_4$. Calculated %: N 12.44.

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CHARACTERISTICS OF THE EFFECT OF SILYL GROUPS:

CHLORINATION OF ALKYLCHLOROSILANES

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The effect of the nature of silyl and germyl groups R_3M (M = Si or Ge), when R is an alkyl or aryl radical, on the chemical and physical properties of organosilicon and germanium compounds has been studied repeatedly. Silyl or germyl groups containing hydrogen atoms or halogens $R_nX_{3-n}M$(X = H, F, Cl, Br) have been studied much less or not at all in this connection [1-10]. By systematically studying the effect of these particular groups we were able to establish some general characteristics of their effect on the physical and chemical properties of a series of organic hydrides and halides of silicon and germanium [5-8]. These characteristics are mainly connected with the inductive effect of the silyl or germyl group on the properties of bonds both adjacent to and more remote from silicon. At the same time, we found that the steric effect of atoms and groups attached to silicon and germanium, which was also noted in the case of R_3M groups, had a definite role in the radical and electrophilic reactions studied. Finally, the reactivities of the compounds we studied, as well as of the compounds containing R_3M, depend on the capacity of Si and Ge to form coordination bonds (with the participation of 3d-orbits).

TABLE 1

"Competing" Photochemical Chlorination of Alkylchlorosilanes by SO_2Cl_2 at 37-40°

	A. $(C_2H_5)_2SiH$ B. Cl_3SiH	A. $(C_2H_5)_3SiH$ B. CH_3SiHCl_2	A. $(C_2H_5)_3SiH$ B. $(CH_3)(C_2H_5)SiHCl$	A. $(CH_3)(C_2H_5)_2SiH$ B. $(CH_3)(C_2H_5)SiHCl$	A. $C_2H_5SiHCl_2$ B. Cl_3SiH	A. $(C_2H_5)_2SiH$ B. $(C_2H_5)_2SiH_2$
Yield of chlorination products of A, %	90	84	69	86	5	82
Yield of chlorination products of B, %	0	0	Less than 20	Less than 8	0	55 $(C_2H_5)_2SiHCl$ 10 $(C_2H_5)_2SiCl_2$
Amount of unreacted A, %	0	0	Less than 20	Less than 7	60	0
Amount of unreacted B, %	50	89	57	69	85	0

Developing this theme in the present investigation, we first examined the photochemical chlorination of alkylchlorosilanes of the series: $(C_2H_5)_2SiH_2$, $(C_2H_5)_3SiH$, $(CH_3)(C_2H_5)_2SiH$, $(CH_3)(C_2H_5)(Cl)SiH$, $(C_2H_5)(Cl)_2SiH$, $(CH_3)(Cl)_2SiH$, and Cl_3SiH with SO_2Cl_2 under conditions recently developed by Voronkov and Davydova [11]. Secondly, we wished to study the effect of the electronegativity of chlorine atoms and of alkyl and aryl groups on the vibration frequencies of Si–H bonds in some silicon mono- and dihydrides.

On the basis of results we obtained previously on the orienting and stabilizing effects of $R_n(X)_{3-n}Si$ groups, we might have expected that on going from $(C_2H_5)_3SiH$ to Cl_3SiH, the rate of the photochemical chlorination of Si–H bonds of the given silane series would decrease sharply. This was actually the case as shown by the data in Table 1 on the "competing" chlorination of these silanes.

Thus, the order of relative activity of these compounds coincides completely with the order of increasing electronegativity of the silyl groups (see Table 2).

TABLE 2

Silane	X_S	ν_{Si-H}, cm^{-1} exper.	calc.	Δ	Source
Cl_3SiH	2,235	2257	2260	−3	[8]
CH_3SiHCl_2	2,188	2214*	2212	+2	Our experiment
$C_2H_5SiHCl_2$	2,182	2204	2206	−2	[8]
$(CH_3)_2(C_2H_5)(Cl)SiH$	2,135	2161*	2158	+3	Our experiment
$(C_2H_5)_2(CH_3)SiH$	2,082	2103*	2105	−2	" "
$(C_2H_5)_3SiH$	2,076	2098	2099	−1	[8]
$(C_2H_5)(C_3H_7)_2SiH$	2,078	2100*	2101	−1	Our experiment
$(CH_3)(CF_3CH_2CH_2)(Cl)SiH$	2,149	2170*	2173	−3	" "
$(F_3CCH_2CH_2)(CH_3)SiH_2$	2,121	2148*	2144	+4	" "
$(mCF_3C_6H_4)(CH_3)SiH_2$	2,126	2152*	2149	+3	" "
$(p\text{-}CH_3C_6H_4)(CH_3)SiH_2$	2,115	2143*	2138	+5	" "
$(CH_2{=}CH)(CH_3)SiH_2$	2,117	2144*	2140	+4	" "
$(C_2H_5)_2SiH_2$	2,101	2130*	2124	+6	[7]
$(F_3CCH_2CH_2)_2SiH$	2,118	2139*	2141	−2	Our experiment

*The Raman spectra of the hydrides were plotted by N. S. Andreev and we would like to express our thanks to him.

It is noteworthy that only the Si–bonds were chlorinated and not the C–H bonds of the alkylchlorosilanes, although it is known [11], that in principle the latter may also be chlorinated under these conditions. As has been already reported [12], this difference in the behavior of Si–H and C–H bonds is due to the characteristics of the Si–H bond and of the silicon atom itself, which, in contrast to carbon, has a highly electrophilic nature (participation of Si 3d-orbits in the formation of the intermediate complex).

From these data one might expect that photochemical radical chlorination of diethylsilane with SO_2Cl_2 should result mainly in the formation of $(C_2H_5)_2SiHCl$. This could occur as a result of the differences in the indictive and steric effects of chlorine* and hydrogen atoms and alkyl groups connected to Si. Actually, chlorination of $(C_2H_5)_2SiH_2$ gave only diethylchlorosilane. We obtained an analogous result from the "competing" chlorination of a mixture of $(C_2H_5)_2SiH_2$ and $(C_2H_5)_3SiH$.

It is difficult to separate the inductive, steric, and other effects of $R_nX_{3-n}Si$ groups by means of data on reactivity. To a certain extent, the solution of this complicated problem could be aided by data on the vibration frequencies of Si–H bonds, which, as we had demonstrated previously [7, 8], are sensitive to changes in the indictive effect of atoms and groups attached to silicon. In our opinion, the conversion from vibration frequencies to electronegativities could be achieved most accurately by using the group electronegativities of silyl groups. Such an empirical method was proposed in 1957 [13]. On the basis of this we recently derived [14] a simpler empirical relation between vibration frequencies (ν) and the values of silyl group electronegativities, namely, $\nu = A \cdot X_S$ where ν is the valence vibration frequency of Si–H and Si–D bonds, A is a constant equal to 1011 for silanes and 734 for deuterosilanes, and X_S is the effective electronegativity of the silyl group. Here, the silyl group electronegativity is considered to be the sum of the effect of the three substitutents attached to Si. By using this equation and reliable data on the vibration frequencies of Si–H bonds from the literature, as well as those we obtained for the silanes investigated, we can express the effect of substitutents in a quantitative form, namely:

*The effect of chlorine atoms attached to Si is seen not only in the strengthening of Si–H bonds, but also in their strong repulsion from the reaction center of the chlorine atoms and ions producing the reaction.

C_6H_{11} (0,684)	iso C_3H_7 (0,687)	C_2H_5 (0,692)	$C_3H_7-C_6H_{13}$ (0,693)	CH_3, (0,698)	
p-$CH_3C_6H_4$, (0,700)	C_6H_5 (0,701)	$CH_2=CH-$ (0,702)			
$F_3CCH_2CH_2-$ (0,706)	m-$CF_3C_6H_4$ (0,711)	$ClCH_2$ (0,717)	H (0,717)		
Br (0,737)	Cl (0,745)	F (0,753)	CN (0,759)	HF_2CF_2C- (0,770)	

The effective electronegativity of other silyl groups is determined by adding these values for the three substituents included in the given silyl group. The values of the vibration frequencies of Si–H or Si–D bonds are readily found by the equation given above. The data in Table 2 show that the values thus calculated for the vibration frequencies of Si–H bonds agree quite well with those found experimentally.

EXPERIMENTAL

1. Di-(m-trifluoromethylphenyl)-silane (I) was prepared by the reaction of the Grignard reagent prepared from 98 g of m-bromobenzotrifluoride and 16.1 g of magnesium in ether, with 13 g of dichlorosilane for one hour at −5°. The mixture was boiled for 1 hour, decomposed with water and treated in the usual way to yield 25.8 g of product (I) (63%), with b. p. 125-126° (12 mm), n_D^{20} 1.4806; d_4^{20} 1.2927. MR_D found 70.46; calculated 70.62.

Found %: C 51.93; 51.70; H 3.18; 3.12; F 35.82; 35.34. $C_{14}H_{10}F_6Si$. Calculated %: C 52.50; H 3.15; F 35.69.

The reaction products also yielded 0.7 g of m-$CF_3C_6H_4COOH$ with b. p. 125-126° (12 mm), and m. p. 104° (from alcohol), whose formation is difficult to explain. The valence vibration frequency in the Raman spectrum of the Si–H bond (ν_{Si-H}) in (I) was 2161 cm^{-1}.

2. Di-p-tolylsilane (II) was prepared under the conditions of experiment 1 from 119.7 g of p-bromotoluene, 19.44 g of magnesium, and 28.5 g of dichlorosilane in ether. The yield of (II) was 46 g (74%), b. p. 137-139° (6 mm), n_D^{20} 1.5731; d_4^{20} 0.9836. MR_D found 71.14; calculated 70.44.

Found %: C 79.16; 79.20; H 7.34; 7.43; Si 13.30; 13.43. $C_{14}H_{16}Si$. Calc. %: C 79.19; H 7.60; Si 13.21.

A small amount of p-$CH_3C_6H_4-C_6H_4CH_3$-p with m. p. 120-123° (from alcohol) was also obtained.
ν_{Si-H} for (II) equalled 2143 cm^{-1}.

3. Bis-(γ,γ,γ-trifluoropropyl)-silane (III) was prepared from 38.3 g of 3-chloro-1,1,1-trifluoropropane, 12.2 g of magnesium, and 21.8 g of dichlorosilane in ether. The yield was 8.7 g (27%) and the product had b. p. (III) 45.5° (33 mm), n_D^{20} 1.3436; d_4^{20} 1.1928. MR_D found 39.78; calculated 40.24.

Found %: C 32.21; 32.08; H 4.32; 4.55; F 50.70; 51.03. $C_6H_{10}F_6Si$. Calculated %: C 32.14; H 4.50; F 50.84.
ν_{Si-H} for (III) equalled 2152 cm^{-1}.

4. Methyl-(m-trifluoromethyl)-phenylsilane (IV) was prepared under the conditions of experiment 1 from 67.5 g of m-bromobenzotrifluoride, 11.9 g of magnesium, and 26 g of methylchlorosilane in ether. The yield was 32.5 g (57%) and the b. p. of (IV) was 43° (15 mm), n_D^{20} 1.4460; d_4^{20} 1.2042. MR_D found 45.91; calculated 46.08.

Found %: C 50.61; 50.55; H 4.92; 4.85; F 28.53; 28.90. $C_8H_9SiF_3$. Calculated %: C 50.51; H 4.77; F 29.97.

ν_{Si-H} for (IV) equalled 2152 cm^{-1}.

5. Methyl-p-tolylsilane (V) was prepared from 96 g of p-bromotoluene, 17.01 g of magnesium, and 35 g of methylchlorosilane. The yield of (V) was 36 g (60%). The b. p. was 63° (18 mm), n_D^{20} 1.5109; d_4^{20} 0.8817. MR_D found 46.28; calculated 45.99.

Found %: C 70.77; 70.68; H 8.77; 8.73; Si 20.00; 20.00. $C_8H_{12}Si$. Calculated %: C 70.53; H 8.88; Si 20.59.

ν_{Si-H} for (V) equalled 2143 cm^{-1}. Crystalline bi-p-tolyl (17.2 g) was also isolated.

6. Methyl-γ,γ,γ-trifluoropropylsilane (VI) was prepared from 39.8 g of 3-chloro-1,1,1-trifluoropropane, 12.16 g of magnesium, and 25.3 g of methylchlorosilane in ether. The yield was 22 g (51%) and the b. p. 58.2° (759 mm), n_D^{20} 1.3408; d_4^{20} 0.9802. MR_D found 30.47; calculated 30.89.

Found %: C 34.02; 33.73; H 6.33; 6.33; F 39.92; 40.40. $C_4H_9SiF_3$. Calculated %: C 33.79; H 6.38; F 40.09.

ν_{Si-H} for $(CH_3)(F_3CCH_2CH_2)SiH_2$ equalled 2148 cm^{-1}.

7. Methylvinylsilane (VII). Over a period of 1 hour, a solution of 25.4 g of methylchlorosilane in tetrahydrofuran was added to vinylmagnesium bromide, prepared from 40 g of vinyl bromide and 9.7 g of magnesium in tetrahydrofuran. When the reaction was complete (at room temperature), the solvent was removed with the low-boiling products by distillation. We isolated 9 g (40%) of (VII) with b. p. 13.7° (757 mm), n_D^4 1.3920; d_4^4 0.6769; MR_D found 25.38, calc. 25.70. ν_{Si-H} for (VII) equalled 2144 cm^{-1}.

8. "Competing" chlorination of silanes. Freshly distilled sulfuryl chloride and silanes were used for the reaction. The molar ratio of silane (A) to silane (B) to SO_2Cl_2 was 0.25:0.25:0.25 the exception of the mixture of $(C_2H_5)_3SiH$ and $(C_2H_5)_2SiH_2$, where A to B to SO_2Cl_2 was 0.2:0.2:0.4 moles. The reagents were loaded in a quartz flask fitted with a thermometer and reflux condenser. The mixture was heated to 37-40° and irradiated with a PRK-4 mercury lamp. Cessation of gas evolution indicated the end of the reaction (3-5 hours). SO_2 was removed from the product mixture on a gas column and the residue was distilled on a normal column. The distillation results are given in Table 1.

Vigorous chlorination occurred when 8 g (0.09 mole) of $(C_2H_5)_2SiH_2$ was mixed with 14 g of SO_2Cl_2. The sole chlorination product was $(C_2H_5)_2SiHCl$ (41%). A minute amount of diethyldichlorosilane was formed.

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HYDROLYSIS OF p-NITROPHENYL ESTERS OF GLYCINE, GLYCYLGLYCINE, AND DIGLYCYLGLYCINE AND THEIR CARBOBENZOXY DERIVATIVES

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Cyanomethyl, p-nitrophenyl, thiophenyl, and other "activated" esters of α-amino acids and peptides are used widely in peptide synthesis [1, 2]. A large number of complex and biologically valuable peptides have been synthesized through activated esters of α-amino acids and peptides. In particular, a nonapeptide with oxytotic activity (oxytocin [3]) was synthesized in this way. Intramolecular condensation of activated peptide esters is a convenient method for preparing cyclic peptides [5]. For example, this method was used to synthesize gramicidin C^4 [T. N. probably C^{14}], an antibiotic which has a cyclic decapeptide structure. In addition, activated peptide esters may be used as monomers in polycondensation reactions for the preparation of high-molecular peptides with a regular sequence of amino acids [6].

In recent years, p-nitrophenyl esters of amino acids and peptides have been used increasingly in peptide synthesis due to their relatively simple preparation and a number of other features. These compounds have attracted further interest as the p-nitrophenyl esters of amino and other organic acids were found to be non-specific substrates for a series of hydrolytic enzymes. p-Nitrophenyl esters of N-carbobenzoxy derivatives of glycine and tyrosine and acetic and other organic acids are also substrates of trypsin, chymotrypsin, thrombin, and other esterases [7]; p-nitrophenyl esters of sulfuric and phosphoric acids are hydrolyzed vigorously by some phosphatases [8] and sulfatases [9].

The use of p-nitrophenyl esters as substrates for esterases was found to be very convenient due to the sharp differences in the positions of the absorption bands of the ester and its hydrolysis product (p-nitrophenol), which made it possible to study the kinetics of enzymic hydrolysis spectrophotometrically. The relative simplicity and accuracy of spectrophotometry made it possible to accumulate a considerable amount of data on the kinetics of esterase action and this has contributed to the recent progress in the study of the mechanism of these enzymes and the structure of their active center [10], containing serine and histidine. As a result of this, the mechanism of imidazole catalysis of ester hydrolysis was discovered and studied [11-13].

As in the synthesis of peptides, one of the main stages in the biosynthesis of protein is the activation of the carboxyl group, but in an aqueous medium under much milder conditions. In biosynthesis, the carboxyl group is activated by the decomposition of aminoacyladenylates which are compounds related and chemically similar to activated α-amino acid esters. Therefore, the study of the reaction of activated esters of α-amino acids and peptides in an aqueous medium under conditions that are close to physiological ones may be used as a model for biosynthetic processes.

The present work was devoted to an investigation of the behavior of the p-nitrophenyl esters of glycine, glycylglycine, and diglycylglycine and their carbobenzoxy derivatives during basic hydrolysis in an aqueous medium.

Due to the very low water solubility of p-nitrophenyl esters, we studied their hydrolysis in an aqueous-alcohol medium (50% by volume) with a constant hydroxyl ion concentration maintained by buffer solutions. The course of the hydrolysis with time was studied spectrophotometrically. From the data obtained we calculated the rate constants for hydrolysis of activated esters and these values were used for evaluating the relative reactivity of the esters. Alcohol solutions of p-nitrophenyl esters of hydrobromides of glycine, glycylglycine, their carbobenzoxy derivatives, and carbobenzoxydiglycine were mixed with equal volumes of phosphate buffer (M/15, pH 7.20), so that the final ester concentration was 10^{-4} M. Before the solutions were mixed, the absorption spectrum of the alcohol solution of the p-nitrophenyl ester was plotted and the absence of the absorption band at λ 315 mμ was considered an indication of the good condition of the ester. Solution of the hydrobromide of the p-nitrophenyl ester of diglycylglycine required preliminary heating which was accompanied by some hydrolysis and the extent of this was measured from the absorption spectrum, as for the concentration of the ester that was not hydrolyzed in alcohol. As heat was evolved when the alcohol solution of activated ester was mixed with the buffer solution, the mixing was carried out at 24.5° so that the whole experiment proceeded at 25°.

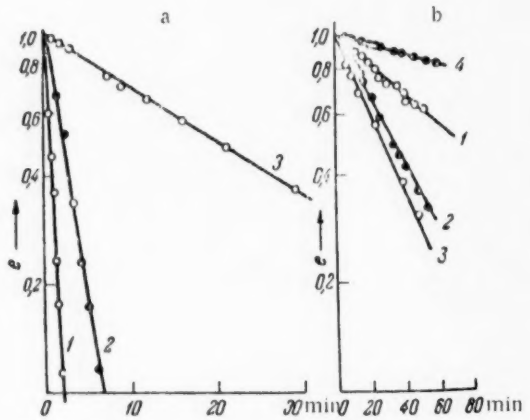

Fig. 1. Hydrolysis of p-nitrophenyl esters of hydrobromides (a) and carbobenzoxy derivatives (b) of: 1) glycine, 2) glycylglycine, 3) diglycylglycine, 4) p-nitrophenyl acetate; in a phosphate buffer (pH 7.2) alcohol (1 : 1) system; at 25° e = 1 −e' is the concentration of p-nitrophenyl esters relative to their initial concentration.

After the alcohol and buffer solutions had been mixed, the mixture was shaken vigorously and transfered immediately to an SF-4 spectrophotometer cell. A mixture of equal volumes of alcohol and phosphate buffer were in the second cell. Both cells were first placed in a copper block, thermostatted at 25°, situated in the cell section of the spectrophotometer. The time from mixing of the reaction mixture components to taking of the first reading did not exceed 30-40 sec. Measurements were taken at a wavelength of λ = 405 mμ which corresponds to the absorption maximum of the p-nitrophenolate ion. The extent of hydrolysis was calculated by the formula $e = (E_m - E(t))/E_m$ where E is the optical density of the solution and the index m indicates completed hydrolysis (maximum optical density). A semilogarithmic plot of the time dependence of e showed that hydrolysis of p-nitrophenyl esters was a first order reaction, as might be expected for solutions with a constant hydroxyl ion concentration. From the data given in Fig. 1, we calculated the experimental hydrolysis rate constants (Table 1). The hydrolysis of p-nitrophenyl acetate (NPA) was studied under the same conditions and the rate constant measured $k_{NPA} = 5.75 \cdot 10^{-5}$ sec^{-1}.

The data we obtained on the hydrolysis rate of p-nitrophenyl acetate agreed with the data of other authors. Bender and Turnquest [11] obtained the value $k_{NPA} = 5.75 \cdot 10^{-5}$ sec^{-1} when studying the hydrolysis of p-nitrophenyl acetate in an imidazole buffer with pH 7.15 at 26.2° in 5% dioxane. Koltun, Dexter et al., [13] obtained the value $k_{NPA} = 1.92 \cdot 10^{-5}$ sec^{-1}, in a phosphate buffer with pH 7.27 at 25° in 2% alcohol. For phosphate buffers in 28.5% alcohol at 25° Bruice and Schmir [12] obtained the value $k_{NPA} = 1.14 \cdot 10^{-5}$ sec^{-1} at pH 6.9 and $k_{NPA} = 4.50 \cdot 10^{-5}$ sec^{-1} at pH 7.4. The somewhat high value, $k_{NPA} = 5.75 \cdot 10^{-5}$ sec^{-1} obtained in the present work can probably be explained by an increase in the hydrolysis rate of p-nitrophenyl acetate due to the higher alcohol concentration in the reaction mixture.

A fall in the stability of ester groups (unactivated) on going from carboxylic acids to amino acids has been reported several times in the literature, but up to now there have been no quantitative data on this problem. The data we obtained for activated p-nitrophenyl esters of amino acids and peptides agree with these qualitative observations. As might have been expected, the hydrobromide of the p-nitrophenyl ester of glycine was hydrolyzed most rapidly of all the compounds studied; removal of the amino group from the hydrobromide

TABLE 1

Relative Hydrolysis Rate of p-Nitrophenyl Esters in the System Alcohol-Phosphate Buffer (M/15) pH 7.20, (1:1) at 25°.

p-Nitrophenyl ester	k, sec^{-1}	k/k NPA
Hydrobromide of glycine	$1{,}46 \cdot 10^{-2}$	$2{,}54 \cdot 10^{2}$
glycylglycine	$5{,}90 \cdot 10^{-3}$	$1{,}09 \cdot 10^{2}$
diglycylglycine	$7{,}84 \cdot 10^{-4}$	$0{,}136 \cdot 10^{2}$
N-Carbobenzoxy-glycine	$1{,}51 \cdot 10^{-4}$	2,63
glycylglycine	$3{,}19 \cdot 10^{-4}$	5,57
diglycylglycine	$3{,}84 \cdot 10^{-4}$	6,67

of the ester of glycylglycine resulted in a decrease in the hydrolysis rate by a factor of 2.5 and in the case of the tripeptide, by a factor of about 19.

Thus, with elongation of the peptide chain the effect of the amino group decreases while the stability of the ester increases and approaches that of carboxylic esters. An inverse relation is observed in the N-carbobenzoxy derivative series: The stability of the p-nitrophenyl esters falls when the carbobenzoxyl group is removed (on going from glycine to dipeptide and tripeptide). On going from glycine to the peptides, the hydrolysis rate increases appreciably (however, this difference is less marked than in the case of hydrobromides), but the difference in the hydrolysis rates of the peptides in comparatively small. It should be noted that the difference in the hydrolysis rates of p-nitrophenyl esters of hydrobromides and the corresponding N-carbobenzoxy derivatives decreases with elongation of the chain. The ratio of the corresponding rate constants for glycine is 96.5, while it is 18.3 for glycylglycine and only 2.05 for diglycylglycine.

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TAUTOMERISM OF AMIDES

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Amides of carboxylic acids show the tautomerism $R-CONH_2 \rightleftharpoons R-C(OH)=NH$. Although various investigators have used chemical and also physical methods (refractometry, ultraviolet and infrared spectra, dipole moments, Raman spectra), there is no single opinion on the structure of amides. In this connection we can, for example, refer to the directly contradictory conclusions of Hantzsch [1] and Grob and Fischer [2]. Up to to now, there have been no cases where two forms of amides have actually been isolated.

We obtained new data on the tautomerism of amides when investigating the rotation dispersion of some derivatives of optically active α-phenylethylamine in the ultraviolet spectrum region using a simple modification of a photoelectric spectropolarimeter designed in our laboratory.

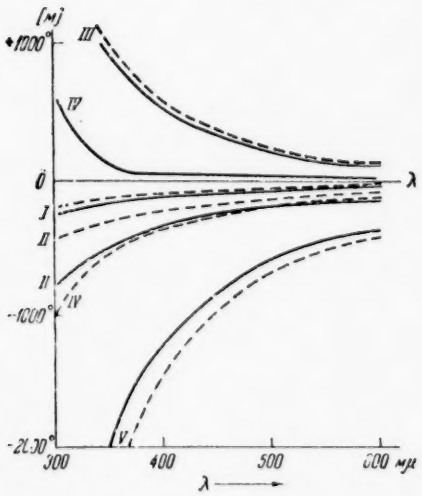
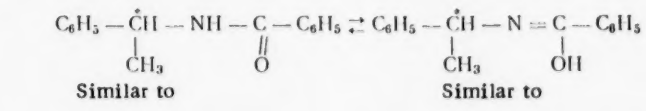


Fig. 1.

The rotation dispersion curves changed little for a free α-phenylethylamine (I), N-benzyl-α-phenylethylamine (II), and benzal-α-phenylethylamine (III) on going from benzene to methanol solutions. In contrast to this, in the case of N-benzoyl-α-phenylethylamine (IV) the sign of rotation and the course of the dispersion curve in benzene (broken line) and in methanol (solid line) are direct opposites (Fig. 1): in benzene, IV shows similarity to II and in methanol, to III, i.e., the lactam form apparently predominates in benzene and the lactim in methanol (cf. data of Yu. N. Sheinker on amino derivatives of pyridine and thiazole [3]).



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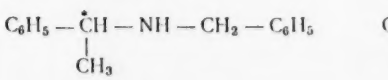

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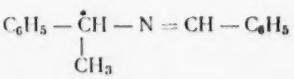

In agreement with this argument, the solvents do not have such an effect on the benzoyl derivative of amine II (Fig. 1, V), as there is no H atom at the nitrogen capable of tautomeric transfer.

These data compelled us to examine anew the information found in the literature on the difference in melting points of benzoyl-α-phenylethylamine: 122° (from alcohol) and 125° (from ligroin) [4,5]. It was found that if a preparation, recrystallized from heptane and having m. p. 128-129°, was heated for a certain time in

dilute methanol, when the solution cooled, it deposited a form with m. p. 123°. On examining the melting process under a microscope, we could observe that the substance which melted at 123° again solidified in spite of the slow rise in temperature, and then melted again at 128°. Apparently, we observed here for the first time the transition of one tautomeric form into another, namely, the labile lactim (m. p. 123°) to the stable lactam (m. p. 128°).

The spectropolarimetric method undoubtedly will be a valuable means of studying other cases of tautomerism. At the present time, we are continuing our study of the behavior of amides and also of compounds of the aminocrotonic ester type.

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REACTION OF UNSATURATED NITRO COMPOUNDS WITH ORGANIC BASES

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Nitroolefins with a nitro group at the unsaturated carbon atom contain a conjugated double bond system capable of adding substances containing a labile hydrogen atom, for example, alcohols, bisulfite, hydrocyanic acid, organic bases, etc. The reaction proceeds according to the scheme

$$>C=CHNO_2 + RH \rightarrow >\underset{R}{C}-\underset{H}{C}=N\begin{matrix}\nearrow O\\ \searrow OH\end{matrix} \rightarrow >\underset{R}{C}-CH_2NO_2.$$

Posner [1] was the first to observe the reaction of unsaturated nitro compounds with organic bases. By treating ω-nitrostyrene with an alcohol solution of hydroxylamine, Posner obtained α-nitro-β-phenyl-β-hydroxylaminoethane as a crystalline substance, which was readily soluble in dilute HCl and dilute NaOH. The reaction of β-nitrostyrene with organic bases was investigated thoroughly by Worrall [2], who established that nitrostyrene reacts with the following bases: aniline, p-toluidine, phenylhydrazine, diphenylhydrazine, β-naphthylhydrazine, p-tolylhydrazine, semicarbazide, thiosemicarbazide, and piperidine.

Wieland and Sakellarius [3] were the first to prepare the addition product of aniline and the lowest nitroolefin, namely, nitroethylene. Later, Heath and Rose [4] gave data on the addition of ammonia, diethylamine, and aniline to the lower nitroolefins, nitroethylene, nitropropylene, and nitrobutylene. A few years ago, in connection with an investigation of cyclohexene nitration, we prepared for the first time the addition product of semicarbazide and an unsaturated nitro compound of the naphthene series, namely, to 1-nitrocyclohexene [5]. For a more detailed study of the reaction of unsaturated nitro compounds of the naphthene and olefin series with organic bases, we investigated the reaction of 1-nitrocyclohexene with the following organic bases: phenylhydrazine, urea, thiosemicarbazide, hydroxylamine, aniline, and p-toluidine.

The investigation showed that aniline and hydroxylamine did not form crystalline derivatives when treated with 1-nitrocyclohexene. Treatment of 1-nitrocyclohexene with phenylhydrazine, urea, thiosemicarbazide, and p-toluidine gave new, crystalline compounds, namely, 2-nitrocyclohexylphenylhydrazine, 2-nitrocyclohexylurea, 2-nitrocyclohexylthiosemicarbazide, and 2-nitrocyclohexyl-p-toluidine.

Treatment of nitroisobutylene with semicarbazide and phenylhydrazine gave crystalline addition products, nitroisobutylsemicarbazide, and nitroisobutylphenylhydrazine.

EXPERIMENTAL

As we reported previously in [5], treatment of 1-nitrocyclohexene with an alcohol solution of semicarbazide acetate gave 2-nitrocyclohexylsemicarbazide, which was the crystalline addition product of semicarbazide and 1-nitrocyclohexene. The yield of the semicarbazide derivative was 75% of theoretical.

In the present work we showed that by using free semicarbazide, instead of semicarbazide acetate, the yield of 2-nitrocyclohexylsemicarbazide could be raised to 89% of theoretical. The starting 1-nitrocyclohexene was synthesized by the method of Levy, Baldock, and Scaife [6]. The constants of 1-nitrocyclohexene were as follows: b. p. 71.5° (3 mm), n_D^{20} 1.5051; d_4^{20} 1.1280; MR found 33.43 (calculated 32.85).

1-Nitrocyclohexylsemicarbaizde. A saturated aqueous solution of KOH (calculated on 0.9 g of KOH) was added to 1.75 g of semicarbazide hydrochloride. The free semicarbazide which separated was dissolved in methyl alcohol and sucked off from the KCl precipitate. The filtrate was added to 1 g of nitrocyclohexene. Mixing of the liquids was accompanied by heat evolution. A white, finely crystalline deposit started to separate immediately and in half an hour the whole mass crystallized. The 2-nitrocyclohexylsemicarbazide crystals were removed by filtration the following day, washed carefully with water and ethyl ether, and dried in a desiccator over $CaCl_2$. The precipitate weighed 1.4 g, which is 89% of theoretical. 2-Nitrocyclohexylsemicarbazide melted with decomposition at 162-162.5°. After recrystallization from ethyl alcohol, the compound had m. p. 163°. Found N 28.15%; calculated 27.73%.

2-Nitrocyclohexylphenylhydrazine. A solution of 1.1 g of phenylhydrazine in 2 ml of ethyl alcohol was added to 0.63 g of 1-nitrocyclohexene. The mixture became orange and quite strong heat evolution was observed. After a few minutes, lustrous, yellow crystals began to form. The following day 0.85 g of precipitate was collected. After another day, a further 0.18 g of crystalline substance precipitated. After recrystallization from ethyl alcohol, the crystals melted at 115-115.5° to give a yellow liquid. The 2-nitrocyclohexylphenylhydrazine, purified by recrystallization, formed a finely crystalline, slightly yellow powder. The color became stronger on storage. As the color became stronger, the melting point fell. A preparation stored in the light for 2 months became a bright yellow liquid. 2-Nitrocyclohexylphenylhydrazine was soluble in organic solvents and 10% H_2SO_4 and insoluble in aqueous alkali. Solution in 10% alcoholic NaOH gave a yellow color, which indicated the formation of an iso salt.

Mixing equimolecular amounts of an alcohol solution of phenylhydrazine and 1-nitrocyclohexene gave an 88% yield of 2-nitrocyclohexylphenylhydrazine.

Found %: C 61.23; H 7.35; N 18.03. Calculated %: C 61.25; H 7.28; N 17.86.

2-Nitrocyclohexylphenylhydrazine hydrochloride. A 0.1-g sample of 2-nitrocyclohexylphenylhydrazine was dissolved in a few milliliters of ethyl ether. The liquid was cooled with ice water and an ether solution of HCl added to it. A light, amorphous precipitate started to form immediately. The precipitate was collected, washed several times with ether, and recrystallized from a mixture of CCl_4 and C_2H_5OH. When heated, the precipitate gradually darkened and at 138-140° it melted to give a dard red liquid.

Found %: Cl 12.84%. Calculated %: Cl 13.05%.

2-Nitrocyclohexylthiosemicarbazide. Thiosemicarbazide (0.46 g) was dissolved with heating in 15 ml of a mixture of water and ethyl alcohol (2:1). The warm solution was added to 0.63 g of 1-nitrocyclohexene. When the mixture cooled, a finely crystalline precipitate formed. On the following day the precipitate was collected and washed with water and ether. The precipitate melted with decomposition at 153.5°. After recrystallization from ethyl alcohol, the compound had m. p. 155°.

Found %: C 38.31; H 6.58; S 15.36. Calculated %: C 38.52; H 6.46; S 14.69.

The 2-nitrocyclohexylthiosemicarbazide yield was 70% of theoretical.

2-Nitrocyclohexyl-p-toluidine. Mixing equimolecular amounts of 1-nitrocyclohexene and p-toluidine did not give a crystalline addition product. Cooling or prolonged storage of the reaction mixture did not produce crystals.

Addition of conc. HCl to the reaction products precipitated 2-nitrocyclohexyl-p-toluidine hydrochloride. A crystalline base was prepared by neutralizing the HCl salt with 1 N NaOH solution.

2-Nitrocyclohexyl-p-toluidine hydrochloride. A 0.54-g sample of p-toluidine was added to 0.63 g of 1-nitrocyclohexene. When the p-toluidine crystals dissolved, the nitro compound became orange. The following day the liquid became viscous. A short time after 2 ml of conc. HCl had been added to the solution, a light crystalline precipitate of 2-nitrocyclohexyl-p-toluidine hydrochloride started to form. The precipitate weighed

0.82 g. The yield was 60.8% of theoretical. When heated, the precipitate started to darken at 142° and melted at 147-148° to form a black liquid. After recrystallization from a mixture of benzene and C_2H_5OH, the substance melted at 150-150.5°.

Found %: Cl 13.04; N 10.10; C 57.60; H 6.70. Calculated %: Cl 13.09; N 10.25; C 57.67; H 6.70.

2-Nitrocyclohexyl-p-toluidine. Two ml of 1 N NaOH solution was added from a micropipette to 0.1350 g of 2-nitrocyclohexyl-p-toluidine hydrochloride. The crystals were triturated carefully with an alkali solution in a porcelain dish, then collected on a filter and washed with several portions of distilled water. The precipitate was dried in a desiccator to give 0.1070 g of product. The yield was 91% of theoretical. The m. p. of the base was 71°.

Found %: C 66.58; H 7.75; N 11.97. Calculated %: C 66.64; H 7.74; N 11.96.

2-Nitrocyclohexyl-p-toluidine was soluble in 10% H_2SO_4 and insoluble in water and aqueous alkali. It was readily soluble in organic solvents (alcohol, benzene, acetone, and CCl_4).

2-Nitrocyclohexylurea. A solution of 0.6 g of urea in 3 ml of ethyl alcohol was added to 0.63 g of 1-nitrocyclohexene. When the liquids were mixed there was no heat evolved and the sharp smell of 1-nitrocyclohexene did not disappear. After standing for 30 days, the mixture was diluted with water. Yellow drops of oil collected on the bottom of the flask and these crystallized on standing. The crystals were collected and washed with ethyl ether. The m. p. of the substance was 190°. The m. p. rose to 193.5° when the substance was recrystallized from ethyl alcohol. The substance decomposed on melting.

Found %: C 44.83; H 6.94; N 22.52. Calculated %: C 44.91; H 7.00; N 22.45.

2-Nitrocyclohexylurea formed light, white crystals. It was soluble in organic solvents and dissolved in water on heating.

1-Nitroisobutylene was prepared by the method of Levy, Baldock, and Wilder-Smith [7] by elimination of nitrous acid from 2-methyl-1,2-dinitropropane, which was synthesized by treating isobutylene with N_2O_4.

The constants of 1-nitroisobutylene were as follows: b. p. 61-62.5° at 10 mm; n_D^{20} 1.4690; d_4^{20} 1.0423; MR found 27.02 (calculated 25.82).

Found %: C 47.48; H 7.91; N 13.83. Calculated %: C 47.56; H 6.98; N 13.87.

Nitroisobutylsemicarbazide. The theoretical amount of semicarbazide dissolved in methyl alcohol was added to 0.5 g of nitroisobutylene cooled with ice. After a few minutes the reaction mass crystallized. The crystals were collected and washed with ethyl ether. The crystals weighed 0.72 g. The substance had m. p. 129-130.5° and after recrystallization from ethyl alcohol, 132.5-133°. The yield was 82.8%. Nitroisobutylsemicarbazide was soluble in organic solvents.

Found %: C 34.08; H 6.84; N 31.73. Calculated %: C 34.08; H 6.86; N 31.80.

Nitroisobutylphenylhydrazine. A 0.54-g sample of phenylhydrazine was added to 0.5 g of nitroisobutylene. The liquid crystallized a few minutes after the reagents had been mixed. The precipitate was collected and washed with ethyl ether. The precipitate weighed 0.99 g and had m. p. 68.5-69°.

After being washed with ether, the precipitate weighed 0.77 g and had m. p. 71-71.5°. The yield was 72% of theoretical. The substance was soluble in organic solvents.

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REACTION OF ALDEHYDES AND KETONES WITH AMIDES OF PHOSPHOROUS ACIDS

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(Presented by Academician B. A. Arbuzov, January 23, 1960)
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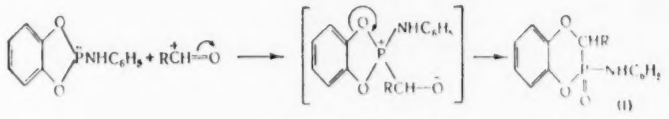
Aldehydes and ketones react with phosphorous esters and dialkylphosphorous acids and form α-alkoxyalkylphosphinic esters in the first case [1] and α-hydroxyalkylphosphinic esters in the second [2]. The reaction of aldehydes and ketones was recently extended to amides of phosphorous acids and it was shown that anilides of phosphorous acids react with aldehydes and ketones to form anilido esters of α-alkoxyalkylphosphinic acids [3] according to the scheme:

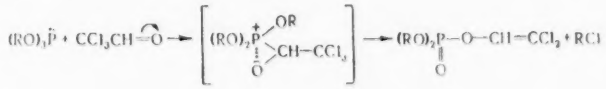


(I)

This reaction course was confirmed by hydrolysis of product I, which yielded pyrocatechol, aniline, and the corresponding α-hydroxyalkylphosphinic acid.

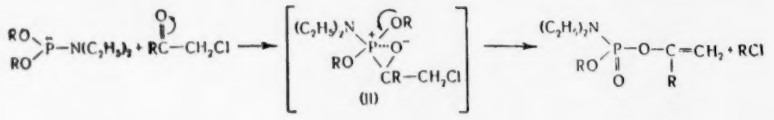
The other possible reaction of aldehydes or ketones with the amido group of amides of phosphorous acids apparently did not occur as no other products, apart from small amounts of tar, were obtained. However, to check the latter statement it was desirable to study the reactions of aldehydes and ketones with disubstituted amides of phosphorous acids. It was found that aldehydes and ketones react with diethylamides of phosphorous acids [4]. Dialkylamides of phosphorous acids react particularly readily with the evolution of heat with halogen-substituted carbonyl compounds such as chloral, chloroacetone, symmetrical dichloroacetone, etc.

As has been shown by a number of chemists [5], esters of phosphorous acid react with halogen-substituted aldehydes and ketones to form mixed esters of phosphoric acid. The primary attack on the phosphite is by the electrophilic carbon atom of the carbonyl group with the formation of an intermediate compound with a three-membered ring and this decomposes with the elimination of alkyl halide and the formation of mixed dialkyl vinyl esters of phosphoric acid according to the scheme:



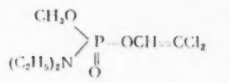
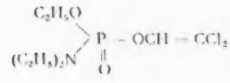
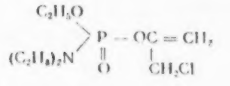
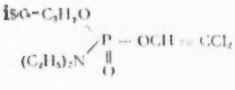
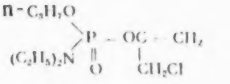
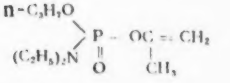
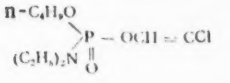
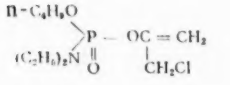
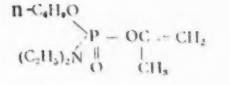
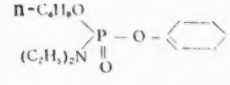
Chloral, chloroacetone, α-chlorocyclohexanone, etc., react readily with diethylamides of phosphorous acids to form amido alkyl vinyl esters of phosphoric acid. The reaction proceeds analogously to the reaction of phosphorous esters and apparently begins with an attack on the phosphorus atom, which bears an unshared pair of electrons, by the electrophilic carbon atom of the carbonyl group with the formation of intermediate

compound (II) and is completed by the conversion to the amido ester of phosphoric acid with the elimination of alkyl halide.



Amido alkyl vinyl esters of phosphoric acid are colorless, mobile liquids, which are almost without smell (see Table 1).

TABLE 1

Formula of amido ester of phosphoric acid	B. p., °C/mm	n_D^{20}	d_4^{20}	*MR* found	*MR* calc.	Yield, %
	116—117/3	1,4646	1,2323	58,79	58,08	60
	112—114/3	1,4600	1,2118	62,33	62,69	62
	120—122/3	1,4545	1,1178	61,98	62,45	78
	124—125/6	1,458	1,1889	66,63	67,31	65
	142—143/10	1,4545	1,0932	66,82	67,05	75
	105—106/5	1,4380	0,9971	61,84	62,29	51
	131—133/3	1,4590	1,1527	72,13	71,93	63
	144—146/5	1,4550	1,0750	71,62	71,68	67
	110—112/4	1,4340	0,9905	66,30	66,82	62
	160—161/6	1,4644	1,0275	77,69	78,47	60

The amido alkyl vinyl esters added bromine. The unsaturation, as determined by the bromide–bromate method for diethylamido butyl isopropenyl ester of phosphoric acid, equaled 100%. When chlorine was present in the vinyl radical, determination of the unsaturation did not give satisfactory results.

Attempts to establish the structure of the products obtained by transesterification [6] did not lead to positive results. When the diethylamido butyl isopropenyl and diethylamido butyl α-methyl-β-chlorovinyl esters of phosphoric acid were boiled with excess butyl alcohol in the presence of sodium alcoholate or phosphoric acid, transesterifiation did not occur and the esters were recovered unchanged from the reaction. Apparently, the presence of a diethylamido group attached to the phosphorus atom has an effect on the transesterification of mixed alkylamido esters. The transesterification is being studied.

Diamido esters of phosphorous acids react with aldehydes and ketones analogously to amido esters.

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*Original Russian pagination. See C. B. translation.

PHYSICOCHEMICAL INVESTIGATION OF THE FORMATION OF FURFURAL – ANILINE RESINS

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(Presented by Academician I. V. Tananaev, January 29, 1960)
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Original article submitted January 20, 1960

The preparation of furfural–aniline resins was described long ago in the literature [1]. They have found application in the preparation of lacquers and in the chemical stabilization of soils [2]. However, the chemistry of the formation of resins from furfural and aniline has not been elucidated in the literature. To study this process, we used physicochemical analysis methods in combination with chemical and physical investigation methods. We examined the light absorption properties of the system, the viscosity, and the heat effect. The starting materials were aniline, furfural, acetone, and toluene (analysis grades) and hydrochloric acid (chemically pure grade). The light absorption of acetone solutions was measured with an SF-4 photoelectric spectrophotometer, the viscosity with a Heppler viscometer (the model for precision measurements), and the heat effect in a calorimeter [3]. The infrared absorption spectra were plotted on an automatic IKS-2 spectrometer. In order to follow the reaction of furfural with aniline at the beginning of resin formation, we investigated the system furfural–aniline–acetone–HCl with the sum of furfural and aniline equal to 20 mol. % and 0.0015 mol. % of HCl.

The light absorption of the system was studied. Acetone solutions of furfural and aniline were mixed in various proportions. HCl was added in the form of concentrated hydrochloric acid to the solutions of aniline in acetone. The light absorption of the solutions was measured half an hour after mixing when it had attained a value which remained constant for a long time.

The results of the measurement are given in Fig. 1. The optical density–composition curve (curve 1, λ = 560 mμ) showed a particular point corresponding to the reaction of furfural with aniline in a molar ratio of 1:1, which showed most clearly in the spectral region of 530-560 mμ. The compound formed from 1 mole of furfural and 1 mole of aniline in the first stage of resin formation corresponds to furfuranil (I) [4].

To study the later stages of resin formation, we investigated the system furfural–aniline–HCl– acetone with the sum of furfural and aniline equal to 20 mol.% and 0.012 mol. % of HCl.

However, in this case, before the preparation of acetone solutions, mixtures of furfural–aniline–HCl of various compositions were heated at 40° for 7 hr. The heating of the furfural–aniline mixtures and the increase in the HCl concentration promoted resin formation. In this case, the optical density–composition diagram (curve 2, λ = 565 m μ) was more complex. The optical density–composition curves showed particular points corresponding to molar ratios of 2:1, 1:1, 1:2, and 1:4. These points were repeated on the optical density–composition diagram for the cross section with a sum of furfural and aniline equal to 40 mol. % (curve 3, λ = 570 mμ).

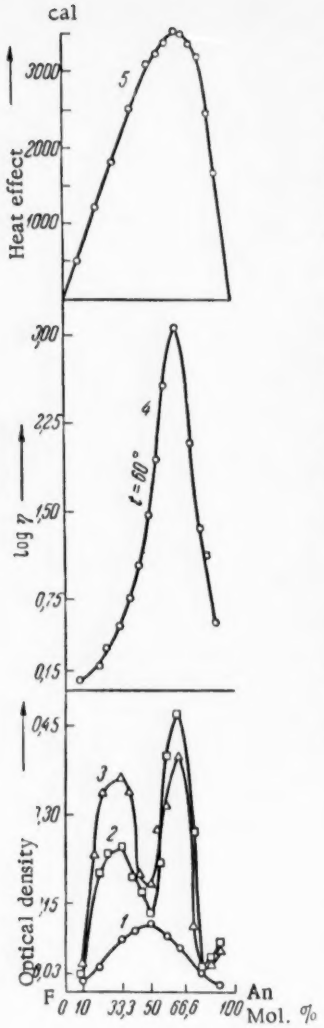


Fig. 1.

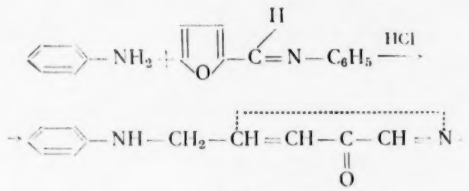
The viscosity of the system furfural–aniline–HCl (0.012 mol.% of HCl) was measured at 60° when the furfural–aniline resins were in a viscous state.

The viscosity–composition curves showed a sharp maximum, corresponding to the reaction of furfural and aniline in a molar ratio of 1 : 2 (curve 4). The viscosity of the system at this point was almost a thousand times that of the starting components. The abscissa (composition) of this maximum remained constant when the system was diluted with an indifferent substance, namely, toluene, although the viscosity of the system was thus decreased.

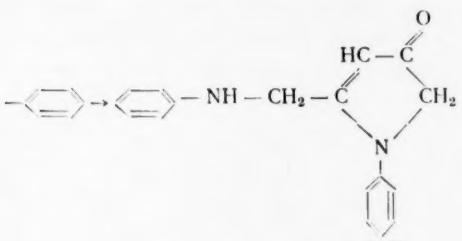
For constructing the heat effect–composition diagram, we studied the system furfural–aniline–HCl (0.048 mol. % of HCl). With a lower HCl content resin formation proceeded slowly and this hampered measurement of the heat effects. The heat effect–composition curve (curve 5) showed a particular point corresponding to reaction of furfural with aniline in a molar ratio of 1 : 2 (the heat effect is expressed in calories per mole of mixture). Thus, the particular point corresponding to the reaction of furfural with aniline in a molar ratio of 1 : 2 was repeated on composition–property diagrams for the properties studied, namely, light absorption, heat effect, and viscosity. Resins corresponding to this composition are the best soil stabilizers [2].

By chemical investigation (analysis, synthesis, and quantitative hydrogenation) and a study of the infrared spectra we established that the given particular point corresponds to two chemical compounds, one of which is converted into the other by cyclization.

On the basis of this, the later stages of resin formation may be represented by the following scheme:



(II)



(III)

We isolated compound III from the resin in the form of colorless crystals with m. p. 144°. It should be noted that this compound was obtained previously under somewhat different conditions by MacGowan. This author assigned to it a formula with a tetrahydropyridine ring [5]. However, when we studied the infrared spectrum of this compound and its hydrogenation product (with 1 mole of H_2) it was found that the absorption frequency of C=O was displaced from the normal value for unstrained rings (1712 cm^{-1}) to a value characteristic of five-membered rings (1742 cm^{-1}) with the simultaneous disappearance of the C=C frequency. It was found that the frequency of the valence vibration of C=O in III was influenced by two effects: on one hand, the conjugation effect which reduced the frequency, and on the other, the strain of the five-membered ring, which increased it. Therefore, the C=O frequency in III has a normal value and does not show conjugation. The ultraviolet spectrum of compound III showed weak conjugation (at λ = 300 mμ the extinction coefficient was reduced from 9100 for III to 4660 for its hydrogenation product).

We were unable to isolate compound II from the resin, but obtained its hydrogenation product (with 1 mole of H_2) in the form of almost colorless crystals (light brown) with m. p. 83-83.5°. The elementary analysis and molecular weight corresponded to the formula $C_{17}H_{18}ON_2$.

The hydrogenation product of III, corresponding to the same empirical formula, had m. p. 114.5-115°. The hydrogenation was carried out under identical conditions in the two cases, namely, over a $Pd/CaCO_3$ catalyst in ethyl acetate at normal pressure and ~18°.

As a result of the investigation it can be considered that furfural–aniline resins (1 : 2 composition) consist of a mixture of low molecular compounds II and III, whose crystallization is hampered by the acyclic form of II.

Our investigation demonstrates the advantage of applying a combination of physicochemical analysis methods and other investigation methods to the study of systems.

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NEW SYNTHESIS OF PHYTOL

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(Presented by Academician B. A. Kazanskii, February 12, 1960)
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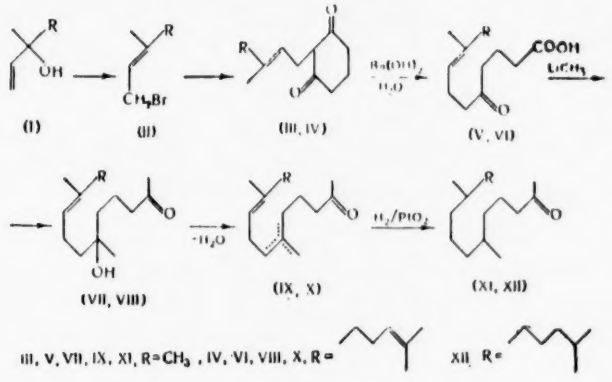
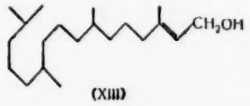
Original article submitted January 19, 1960

In previous work [1] we accomplished the alkylation of dihydroresorcinol by prenyl bromides (II) and hence obtained about 50% yields of a number of cyclic β-diketones containing isoprenoid chains.

In the present article it is shown that these derivatives of dihydroresorcinol may be used for the synthesis of phytol (XIII) and other isoprenoid compounds.





Hydrolytic cleavage of 2-prenyl- and 2-geranyldihydroresorcinols (III) and (IV) gave high yields of the corresponding keto acids (V) and (VI), which reacted smoothly with excess methyllithium with the participation of both functional groups. When the keto alcohols (VII) and (VIII) thus obtained were dehydrated with potassium bisulfate with subsequent exhaustive hydrogenation of the unsaturated ketones (IX) and (X) over platinum oxide, we obtained known ketones, namely, tetrahydrogeranylacetone (XI) and hexahydrofarnesylacetone (XII) [2], which were previously synthesized by other methods. According to [3] and the data of one of us [2], ketone (XII) is readily converted into phytol (XIII).

Thus, we developed a new method of synthesizing isoprenoid compounds which makes it possible to extend the chain of vinyl alcohols (I) by 8 carbon atoms and obtain high yields of ketones of type (XI) and (XII).

EXPERIMENTAL

Preparation of tetrahydrogeranylacetone (XI). A solution of 15 g (0.07 mole) of 5-keto-9-methyl-8-decenoic acid (V) (m. p. 41-42°) in 150 ml of absolute ether was added with stirring to a solution of methyllithium prepared from 5.5 g (0.79 g-at) of lithium, 56.3 g (0.39 mole) of methyl iodide, and 300 ml of absolute ether. The reaction mixture was boiled for 1 hr and then treated with ice. From the ether layer we isolated 15 g of unpurified keto alcohol (VII), containing 98% of carbonyl compound.*

A mixture of the keto alcohol (VII) obtained and 1 g of potassium bisulfate was heated to 120° at a pressure of 60 mm and then the temperature was raised to 160° over a period of 20 min. The dehydration product was diluted with ether and washed with water and after removal of the solvent, we obtained 10.7 g of the unsaturated ketone (IX) with b. p. 107-112° at 7 mm and n_D^{20} 1.4705, containing 85% of carbonyl compound.

Found %: C 80.36; 80.48; H 11.29; 11.53. $C_{13}H_{22}O$. Calculated %: C 80.35; H 11.41.

According to literature data geranylacetone has b. p. 133-135° at 20 mm and n_D^{20} 1.4664 [2].

When 10.9 g of unsaturated ketone (IX) was hydrogenated in methanol over platinum oxide (744 mm, 20°), two equivalents of hydrogen (2.7 liters) was absorbed. As a result we obtained 9.6 g of tetrahydrogeranylacetone (XI) with b. p. 103-108° at 7 mm and n_D^{20} 1.4375, containing 84% of carbonyl compound. The semicarbazone melted at 95-96° and did not depress the melting point of an authentic sample. The following constants are given in the literature [2] for tetrahydrogeranylacetone: b. p. 95-97° at 4 mm, n_D^{20} 1.4334, semicarbazone, m. p. 95-96°.

Preparation of hexahydrofarnesylacetone (XII). To a solution of 350 g of barium hydroxide in 2 liters of water was added 70 g (0.28 mole) of 2-geranyldihydroresorcinol (IV) (m. p. 101-104°) [1] and the mixture boiled with stirring for 12 hr. The reaction mixture was cooled, acidified (to Congo) with concentrated HCl, and extracted with ether to yield 54.4 g of 5-keto-9,13-dimethyl-8,12-tetradecadienoic acid (VI) with b. p. 181-184° at 0.05 mm and n_D^{20} 1.4833.

Found %: C 71.88; 72.24; H 9.84; 9.97. $C_{16}H_{24}O_2$. Calculated %: C 72.14; H 9.84.

The S-benzylthiuronium salt melted at 121-122° (from aqueous methanol).

Found %: N 6.87; 6.83. $C_{24}H_{36}O_3N_2S$. Calculated %: N 6.48.

Analogously, the action of methyllithium [3.26 g (0.48 g-at) of lithium and 33.4 g (0.23 mole) of methyl iodide] on 12.2 g (0.046 mole) of 5-keto-9,13-dimethyl-8,12-tetradecadienoic acid (VI) and subsequent dehydration of the keto alcohol (VIII), containing 97% of carbonyl compound, yielded 9.4 g of unsaturated ketone (X) with b. p. 120-125° at 0.05 mm and n_D^{20} 1.4811, containing 90% of carbonyl compound.

Found %: C 82.03; 82.29; H 11.66; 11.62. $C_{18}H_{30}O$. Calculated %: C 82.38; H 11.52.

According to literature data [2], farnesylacetone has b. p. 143-144° at 0.42 mm and n_D^{20} 1.4810.

A sample of 12.3 g (0.047 mole) of unsaturated ketone (X) was hydrogenated in methanol over platinum oxide (738 mm, 20°). When three equivalents of hydrogen (3.7 liters) had been absorbed, we isolated 12.1 g of hexahydrofarnesylacetone (XII) with b. p. 107-110° at 0.05 mm and n_D^{20} 1.4458, containing 88% of carbonyl compound.

Found %: C 80.80; 80.57; H 13.70; 13.56. $C_{18}H_{36}O$. Calculated %: C 80.52; H 13.52.

The semicarbazone melted at 68-69° and did not depress the melting point of an authentic sample (m. p. 68-69°) [3]. According to literature data [2], hexahydrofarnesylacetone has the following constants: b. p. 120-123° at 1 mm, n_D^{20} 1.4445, semicarbazone, m. p. 69-70°.

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*According to data on oxime formation here and in other cases.

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HYDROGENATION OF 2-METHYL-1-BUTENE IN THE PRESENCE OF PLATINUM BLACK IN A MEDIUM OF DEUTERATED ALCOHOL

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Many investigators of hydrogenation on a platinum catalyst have reported that the nature of the solvent has a substantial effect on the rate and sometimes the direction of this reaction [1-7]. It was shown that in protolytic solvents, as compared with neutral ones, there is a considerable acceleration of the hydrogenation of some compounds and in most cases the accelerating action is proportional to the lability of the hydrogen atom in the solvent molecule. This relation was not observed for a series of other compounds [5-7]. On this basis, some investigators consider that the solvent participates directly in catalytic hydrogenation and is involved in the formation of complex intermediate compounds between catalyst, substance hydrogenated, and hydrogen [4, 8-10].

TABLE 1

Results of Experiments on Isotopic Exchange between Deuterated Alcohol and Substances Involved in the Hydrogenation of 2-Methyl-1-butene on a Platinum Catalyst

Expt. No.	Catalyst sample, g	Pressure, mm Hg	Expt. duration, hr	Monodeutero derivative content, %
4	0,2081	742	3,00	2
5	0,2036	736	2,30	—
6	0,2036	737	2,50	2,2
11	1,1952	746	9,10	2,3
13	0,1957	without H_2	3,00	0,67
14	0,1966	735	1,20	2,4
15	0,2035	without H_2	3,15	0,0
16	0,2084	736	—	3,4

Footnote. The solvent was C_2H_5OH in experiment No. 5. The catalyst from experiment No. 5 was used in experiment No. 6. The exchange of 2-methyl-1-butene with C_2H_5OD was studied in experiment No. 15; 3 ml of isopentane were used. The exchange of H_2 with C_2H_5OD was studied in experiment No. 16; hydrogen was passed at a rate of 6 ml/min.

In the present work we made an attempt to determine whether the hydroxyl hydrogen of the alcohol participated directly in the catalytic hydrogenation. For this purpose, we studied the hydrogenation of 2-methyl-1-butene on platinum black in ethyl alcohol containing 3.3% of deuterium in the hydroxyl group. The hydrocarbon formed was analyzed on a mass spectrometer to determine its deuterium content.

The results of the investigation, which are given in Table 1, show that the hydrogenation yielded isopentane containing about 2.3% of monodeuteroisopentane. Dideuteroisopentanes were not detected. In a control experiment (No. 15) where isopentane was shaken with deuterated alcohol and platinum black in a nitrogen atmosphere at 20° for 3 hr 15 min, no isotopic exchange was observed. This was also confirmed by the results of experiment No. 11, where the deuterium content of the isopentane did not increase after the hydrogenation had been carried out with shaking for 8 hr in a hydrogen atmosphere, although the deuterium content of the hydrogen reached approximately 3.3% under these conditions. In the absence of hydrogen (in experiment No. 13), 2-methyl-1-butene gave 0.67% of monodeuteroolefin. When hydrogen was passed through a hydrogenation flask with deuterated alcohol and platinum black at a rate of 6 ml/min, which corresponded to the rate of its absorption during hydrogenation of 2-methyl-1-butene, the hydrogen was found to contain 3.4% of HD.

Thus, the results obtained show that the exchange of hydrogen with deuterated alcohol occurring on platinum under the given conditions reached equilibrium within the limits of accuracy of the measurements. The extent of isotopic exchange of 2-methyl-1-butene with deuterated alcohols, obtained in the control experiment, equaled 0.67%, which is undoubtedly higher than the fraction that this isotopic exchange reaction contributed to the total deuterium content of the hydrogenation product. The extent of isotopic exchange of the olefin with alcohol was less during the hydrogenation of the olefin as the olefin concentration continuously decreased. The surface concentration of olefin adsorbed on the catalyst was also less during the hydrogenation than in the control experiment due to the adsorption of hydrogen on some of the active centers of the catalyst.

The formation of the monodeuteroparaffin may be explained by the fact that an HD molecule is first formed by isotopic exchange of hydrogen with alcohol and this molecule then adds to the olefin; thus, the hydrogenation and exchange proceed simultaneously and independently. The absence of appreciable amounts of di- and trideuteroparaffins also confirmed this point of view as the probability of the formation of D_2 molecules under these conditions is very small. In addition, this shows that there is practically no exchange of olefin with alcohol during hydrogenation.

It is interesting to note that the exchange of hydrogen with deuterated alcohol gave hydrogen containing 3.4% of HD while the isopentane obtained by hydrogenation containing only 2.3% of monodeuteroisopentane although it would seem that the whole of the HD should add to the olefin. This may be explained by a difference between the rates of exchange of C_2H_5OD with H_2 and hydrogenation of the olefin on the catalyst surface. Hence, it can also be seen that the hydroxyl hydrogen of the solvent alcohol did not participate directly in the hydrogenation.

The hydroxyl hydrogen of the alcohol exchanged with hydrogen adsorbed on the catalyst surface. If there was an olefin in the system, then, being adsorbed on the platinum, it reacted with the adsorbed H_2 and HD. In addition, the olefin reduced the surface concentration of hydrogen and hence the rate of exchange of hydrogen with alcohol.

Thus, the two possible isotope exchange reactions of olefin with alcohol and hydrogen with alcohol and also the hydrogenation of the olefin have a common limiting stage, namely, the adsorption of hydrogen on the platinum. With all these processes proceeding simultaneously, the rate of the exchange reactions decreases; thus, the exchange of hydrogen with the alcohol falls from 3.4 to 2.3%, while the exchange of olefin with alcohol is completely suppressed, as is shown by the absence of dideuteroisopentanes.

EXPERIMENTAL

2-Methyl-1-butene was obtained by dehydration of isoamyl alcohol over aluminum oxide at 400° with subsequent distillation of the dehydration products. The material had b. p. 30.6° (746 mm); d_4^{20} 0.6507, n_D^{20} 1.3774. Literature data [11, 12]: b. p. 31.163° (760 mm); d_4^{20} 0.6504, n_D^{20} 1.3778. The platinum black was prepared by Wilstatter's method [13]. The deuterated alcohol was obtained by isotopic exchange between alcohol and heavy water.

The hydrogenation was carried out in a hydrogenation flask fitted with a thermostatted jacket. A Patrikeev gasometer system with a 1-liter burette was used to maintain a constant hydrogen pressure in the system and measure the hydrogen consumption. To increase the reliability of the operation of this instrument, the circuit of the photoelectronic amplifier was changed as the factory circuit required adjustment during the experiment. The circuit with a cathode follower which was used [15] guaranteed stable operation of the instrument.

The hydrogenation experiments were carried out in the following way: Into the hydrogenation flask was placed 10 ml of alcohol and a sample of catalyst introduced in a stream of nitrogen. The whole system was flushed with hydrogen and 3 ml of isoamylene in 10 ml of alcohol introduced into the hydrogenation flask in a stream of hydrogen. The hydrogenation flask was closed and connected to the gasometer with an excess hydrogen pressure of 30 mm water. The shaker was switched on and the reading on the gasometer simultaneously recorded. All experiments were carried out at 20°. At the end of the experiment the hydrogenation flask was cooled to 10° and its contents poured into a cooled 50-ml flask. The catalyst remained in the hydrogenation flask. The azeotrope of the hydrocarbon and alcohol was distilled on a water bath up to 50° into a receiver tube at −70° and treated twice with equal volumes of concentrated calcium chloride solution. The hydrocarbon obtained was dried over fired calcium chloride and distilled up to 40°. A sample of hydrocarbon (0.3 ml) was

taken from the receiver tube with a Record type medical syringe of 1 ml capacity with a needle. For analysis on a mass spectrometer, the sample was introduced into a previously weighed ampoule, whose lower end was cooled in a mixture of acetone and solid carbon dioxide. The upper end of the ampoule was then sealed and the ampoule and contents weighed.

TABLE 2

Mass Spectra of Isopentane According to [17] and Mass Spectra Obtained in the Present Work (Relative Intensities)

m/e	iso-C_5H_{12} [17], U = 70 v	iso-C_5H_{12}, Exp. No. 5, U = 34 v	iso-C_5H_{12} + iso-$C_5H_{11}D$, Exp. No. 14, U = 36 v	iso-C_5H_{10}, U = 44 v	iso-C_5H_{10} + + iso-C_5H_9D, Exp. No. 13, U = 40 v
26	4,11	1,48	1,9	2,63	2,25
27	42,2	11,7	13,3	16,0	12,0
28	6,17				
29	45,7	27,8	29,8	22,2	21,4
30				7,2	
39	21,5	4,17	5,2	26,5	22,8
40	3,38	1,7	2,0	4,5	4,1
41	67,3	59	62,0	24,4	25,8
42	86,0	92,0	92,0	31,4	33,0
43	100	100	100	3,5	2,6
51				2,0	1,5
52				1,15	1,0
53				8,9	8,4
54				3,2	3,2
55	4,71	4,2	4,2	100	100
56	16,8	18,9	19,3	5,0	5,0
57	54,0	57,0	57,5		
58		0,08	1,3		
69				3,14	3,2
70				38,6	35,8
71	1,82	1,95	2,0		0,24
72	6,19	7,71	7,71		
73			0,19		

Footnote. U is the ionizing voltage.

The isopentane and isoamylene was analyzed mass spectrometrically on an MS-4 instrument. A glass inlet system was used for introducing the sample into the gas ion source of the mass spectrometer. The dosing valve with a needle used made it possible to regulate smoothly the gas stream of sample into the ion source. The small difference in the masses of the molecules analyzed made it possible to ignore the molecular character of the leakage and to use a high pressure (50 mm Hg) before the value [16].

The inlet system with the ampoule in it was pumped out to a pressure of $5 \cdot 10^{-2}$ mm Hg with a fore-vacuum pump and the tap set in such a position that all the openings were covered. The ampoule was broken and the sample evaporated into the buffer volume. The leakage of sample into the ion source was regulated with the dosing valve so that the most intense peak of the spectrum was approximately 20 v. The mass spectrum of the sample investigated was plotted from the output voltmeter of the electrometric amplifier and recorded with an ÉPP-09 automatic potentiometer.

Samples of the spectra obtained with corrections for the natural content of D and C^{13} are given in Table The table does not include the small peak with m/e = 28 with whose measurement the background of the instrument interfered. The spectrum of isopentane was published in [17] and is given for comparison, but it was obtained on a 180° instrument with scanning by the accelerating voltage and therefore it differs very strongly from that which we obtained. The content of deutero-substituted molecules was calculated from the molecular peaks.

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CARCINOLYTIC PEPTIDES WITH A DIRECTED ACTION

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The genetic etiology of cancer leads to the unavoidable conclusion that there is need either for disaggregation of the nuclear DNA of a cancer cell, which is difficult to achieve, or for the application of chemical mutagenic agents which, by acting cytostatically or by producing lethal mutations, make the nearest generations of the cancer cells nonviable. This situation is confirmed by the fact that all the carcinolytic preparations known at the present time (sarcolysin, dopane, embichine, thiotef, etc.), are mutagenic [1, 2]. However, these preparations are nonspecific. Their action hardly differentiates between cancerous and normal cells [3] and as a rule, a consequence of their use is disease of the bone marrow cells. Naturally, the action of the preparations differentiates even less between different strains of cancer. The nonspecificity of separate amino acids bearing a mutagenic group (for example, p-di-(2-chloroethyl)-aminophenylalanine) may be explained by the fact that the DNA of both healthy and cancerous cells have loci for the adsorption of any of the essential amino acids forming the basis of the usual carcinolytic preparations.

The hypothesis that DNA may adsorb short peptides in which the order of linking of the amino acids happens to correspond to the pattern of a definite section of the DNA makes it probable that there will be a higher specificity in the action of peptides, rather than separate amino acids, bearing mutagenic groups.

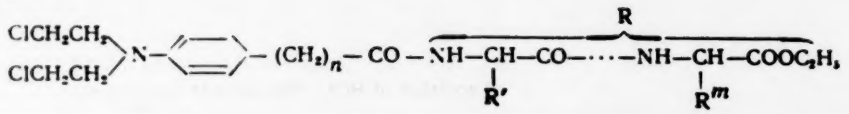
Biological testing of the dipeptides that we obtained previously [4, 5] showed that when they lacked the toxicity inherent in previously known preparations of this group, depending on the terminal amino acid and the structure of the mutagenic group bearer, the compounds had a selective action directed against different strains of malignant tumors [6, 7].

Even higher specificity of action may be expected from tri- and tetrapeptides as, depending on the order of linking and nature of the amino acids, they may have the capacity for specific adsorption on different DNA of cancerous and healthy cells, on the one hand, and on qualitatively different DNA of various strains of cancerous cells, on the other, i.e., that differentiation of action which cannot be achieved by contemporary antitumor preparations.

For this purpose we condensed esters of di- and tripeptides with p-di-(2-chloroethyl)-aminophenylacetic and γ-[p-di-(2-chloroethyl)amino]-phenylbutyric acids to prepare tri- and tetrapeptides bearing a mutagenic group in the acyl residue of the N-terminal amino acid (see Table 1, compounds No. 1-14).

The compounds prepared showed a high selectivity of action in experiments on animals with respect to various strains of cancerous tumors, depending on the nature of the amino acids forming the peptide chain and the nature of the terminal amino acid bearing the mutagenic group [7]. In the case of peptides containing unnatural amino acids, the antitumor action was reduced or disappeared. Thus, the ethyl ester of p-di-(2-chloroethyl)-aminophenacetyl-β,β-ditrifluoromethyl-α-aminopropionic acid (compound No. 17) had no antitumor activity. The percent retardation of sarcoma-45 by the ethyl ester of p-di-(2-chloroethyl)-aminophenacetyl-β-phenyl-β-alanine was only 51%, while for the ethyl ester of p-di-(2-chloroethyl)-aminophenacetyl-β-phenyl-α-alanine it was 98.7%. An antitumor activity was also shown by some amides of p-di-(2-chloroethyl)-aminophenylacetic and γ-[p-di-(2-chloroethyl)-amino]-phenylbutyric acids (compounds No. 22 and 24).

TABLE 1



Sample No.	n	R	M. p., °C	Yield, %	Found, %				Calculated, %			
					C	H	N	Cl	C	H	N	Cl
1	1	Leucylphenylalanine ethyl ester	128—129	51	61,63	7,19		12,31	61,7	6,92		12,59
2	1	Phenylalanylleucine ethyl ester	119—122	61	61,35	6,93		11,60	61,7	6,92		12,59
3	1	Phenylalanylmethionine ethyl ester	139—140,5	57	57,76	6,10	7,37		57,73	6,36	7,22	
4	1	Leucylmethionine ethyl ester	119,5—122	34	54,80	6,98	7,39		54,74	7,12	7,66	
5	1	Phenylalanylphenylalanine ethyl ester	117—120	38	64,35	6,24		12,50	64,21	6,19		11,87
6	1	Leucylleucine ethyl ester	100—104	59	58,48	7,74		13,64	58,87	7,74		13,40
7	1	Phenylalanylvaline ethyl ester	154—156	63	61,21	6,59		12,35	61,09	6,73		12,91
8	3	Phenylalanylleucine ethyl ester	143—144	40	61,92	7,28		11,28	62,84	7,26		11,99
9	3	Phenylalanylphenylalanine ethyl ester	121—125	60	65,06	6,62	6,17		65,18	6,55	6,71	
10	3	Leucylleucine ethyl ester	125—126	31	60,00	7,97		12,15	60,22	8,06		12,72
11	1	Methionylleucylphenylalanine ethyl ester	185—187	24	58,71	6,76	7,87		58,70	6,91	8,06	
12	1	Methionylphenylalanylvaline ethyl ester	184—186	24	58,42	6,57	8,33		58,15	6,75	8,22	
13	3	Methionylleucylphenylalanine ethyl esuer	140—145	33	59,86	7,26	7,73		59,75	7,19	7,74	
14	3	Leucylphenylalanylmethione ethyl ester	165—170	16	59,74	7,29	7,84		59,75	7,19	7,74	
15	1	Proline ethyl ester	81,5—82	86	56,81	6,64	6,79	17,38	56,86	6,48	6,98	17,71
16	1	Dimethyl glutamate	81—82[1]	67	52,42	5,99		16,11	52,66	6,00		16,39
17	1	Ethyl β,β-ditrifluoromethyl-α-aminopropionate (hexafluorovaline)	73—76	46	45,21	4,43	5,85		44,61	4,30	5,47	
18	1	Phenylalanine ethyl ester[4]	81—84[1]	81	62,47	6,79		14,61	62,63	6,68		14,82
19	1	Methionine ethyl ester[4]	93—95[1]	79	53,89	6,91			54,43	6,91		
20	3	Dimethyl glutamate	68—70	86	54,63	6,58			54,66	6,51		
21	3	Ethyl β-aminoenanthate[5]	63—65	25	60,00	7,87	6,05		60,13	7,84	6,1	
22	1	Anesthesin[3]	132,5—135[1]	90	59,82	5,77		16,64	59,57	5,67		16,78
23	1	Threoamine [1-(p-nitrophenyl)-2-amino-1,3-propanediol]	125—128	95	53,58	5,45		14,65	53,62	5,32		15,11
24	1	6-Methoxy-8-aminoquinoline	117—118[1]	93	60,87	5,50		16,21	61,11	5,32		16,44
25	1	Indoline	161[2]	50	63,73	6,03	7,65	18,30	63,66	5,84	7,43	18,83
26	1	Tryptamine	128	41	63,23	6,04	9,98	16,79	63,16	5,98	10,05	16,98
27	3	Anesthesin	116—118[1]	91	61,54	6,54	6,27	15,43	61,20	6,21	6,21	15,74

NOTES TO TABLE 1

Footnote. For the preparation of analogs of tri- and tetrapeptides from intermediate N-formyl derivatives of peptide esters, the formyl group was removed by heating the derivatives for one minute with 6N alcohol solution of HCl. The solvent was removed in vacuum and the residue dissolved in $CHCl_3$ and neutralized with a $CHCl_3$ solution of ammonia. The free base could not be isolated in a pure form. After removal of the $CHCl_3$, the residue was acylated in the usual way with the N-formylamino acids from p-di-(2-chloroethyl)-aminophenylacetic or γ-[p-di-(2-chloroethyl)-amino]-phenylbutyric acids. The general method for the preparation of carcinolytic acylamino acids and peptides bearing di-(2-chloroethyl) amino groups was published previously [4, 5]. DL-Amino acids were used for the reactions. In most cases, the final product was purified by recrystallization from ethyl alcohol

[1]Recrystallized from ethyl acetate–ligroin.

[2]Recrystallized from ethyl acetate.

[3]Darkened on prolonged storage in light.

[4]In this case, instead of p-di-(2-chloroethyl)-aminophenylacetic acid we used p-di-(2-chloropropyl)-aminophenylacetic acid; the latter was obtained in 26% yield by condensation of ethyl p-aminophenylacetate with propylene oxide and subsequent reaction with $POCl_3$. The colorless crystals had m. p. 121-122° (from ligroin).

Found %: C 55.27; H 6.22; Cl 22.23. $C_{14}H_{19}Cl_2NO_2$. Calculated %: C 55.25; H 6.25; Cl 23.28.

According to the preliminary data of L. F. Larionov and S. S. Kyablos p-di-(2-chloropropyl)-aminophenylacetic acid has a high antitumor activity (the percentage retardation reached 98.98% in the case of sarcoma-45).

[5]We isolated a 38% yield of N-p-di-(2-chloroethyl)-amino- γ-phenylbutyryl-1,3-dicyclohexylurea as a by-product.

In order to study the effect of the lability of halogen atoms in the mutagenic group on the antitumor activity of the compounds, we compared the action of similarly constructed peptides bearing di-(2-chloroethyl)- and di-(2-chloropropyl)-amino groups (compounds No. 18 and 19). The antitumor activity was reduced in the case of the latter.* A comparison of the antitumor activity of peptides containing residues of p-di-(2-chloroethyl)-amino-D,L-phenylalanine (sarcolysine) with peptides bearing residues of p-di-(2-chloroethyl)-aminophenylacetic and γ-[p-di-(2-chloroethyl)-amino]-phenylbutyric acids showed that in the case of the latter the spectrum of antitumor activity became wider, while the antitumor activity (in experiments on animals) was not only not reduced, but even exceeded that of peptides containing sarcolysine residues for some strains of cancerous tumors.

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CATALYTIC CONDENSATIONS OF SCHIFF'S BASES FROM 4-AMINOBIPHENYL AND AROMATIC ALDEHYDES WITH ALIPHATIC-AROMATIC KETONES

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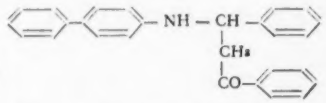
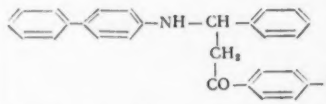
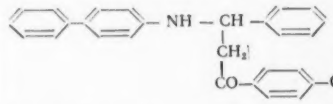
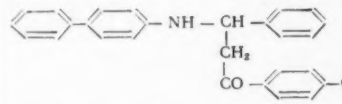
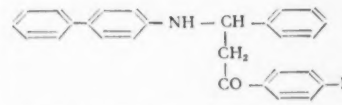
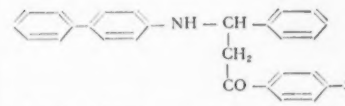
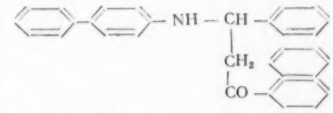
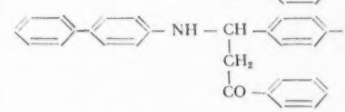
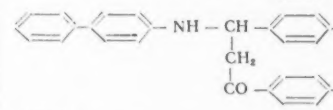
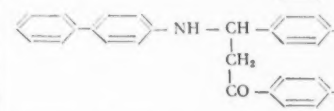
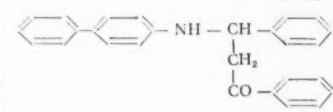
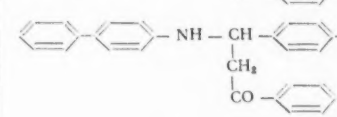
In the work of one of us [1] a method was proposed for the synthesis of β-arylamino ketones by catalytic condensation of Schiff's bases with ketones. The present work is a continuation of this. For the investigation we used Schiff's bases from 4-aminobiphenyl and aromatic aldehydes, which were condensed with a series of aliphatic-aromatic ketones. The purpose of the present work was to prepare new organic compounds with potential physiological activity as it is known that 4-aminobiphenyl and a number of its derivatives have considerable and varied physiological activity. Thus, for example, 4-aminobiphenyl shows a tuberculostatic action even at a concentration of $1.25 \cdot 10^{-7}$ M [2], which is approximately 20 times the activity of such a generally accepted preparation as p-aminosalicylic acid [3].

L. F. Trefilova and I. Ya. Postanovskii [4] synthesized a series of new derivatives of 4-aminobiphenyl, in particular, azomethines and N,N'-substituted thioureas. Some of the azomethines were found to be very active and suppressed the growth of tubercle bacilli at preparation concentrations of $1 \cdot 10^{-6}$ to $1 \cdot 10^{-7}$ M.

For physiological testing, Ch. P. Ivanov and I. M. Panaiotov [5] synthesized a series of alkyl ethers of 4-hydroxy-4-aminobiphenyl and its aminoacetyl derivative. As 4-aminobiphenyl has a high toxicity and is readily oxidized, D. Sh. Rozina and R. P. Lastovskii [6] synthesized 4-aminobiphenyl glucoside and 4-aminobiphenyl-4-acetylaminosalicylic acid. In recent years it has been established that 4-aminobiphenyl has an appreciable carcinogenic action [7, 8].

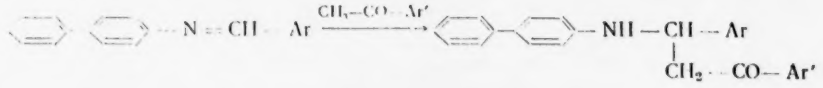
In the present work, benzal-4-aminobiphenyl was condensed with acetophenone to synthesize β-(4-phenylanilino)-β-phenylpropiophenone (I). Condensation of benzal-4-aminobiphenyl with 4-methylacetophenone yielded 4-tolyl β-(4-phenylanilino)-β-phenylethyl ketone (II). Condensation of benzal-4-aminobiphenyl with 4-methoxyacetophenone yielded 4-anisyl β-(4-phenylanilino)-β-phenylethyl ketone (III). Condensation of benzal-4-aminobiphenyl with 4-chloroacetophenone yielded 4-chlorophenyl β-(4-phenylanilino)-β-phenylethyl ketone (IV). Condensation of benzal-4-aminobiphenyl with 4-bromoacetophenone yielded 4-bromophenyl β-(4-phenylanilino)-β-phenylethyl ketone (V). Condensation of benzal-4-aminobiphenyl with methyl biphenylyl ketone yielded 4-biphenylyl β-(4-phenylanilino)-β-phenylethyl ketone (VI). Condensation of benzal-4-aminobiphenyl with methyl α-naphthyl ketone yielded α-naphthyl β-(4-phenylanilino)-β-phenylethyl ketone (VII). Condensation of 4-tolyl-4-aminobiphenyl with acetophenone yielded β-(4-phenylanilino)-β-4-tolylpropiophenone (VIII). Condensation of 4-tolyl-4-aminobiphenyl with 4-methylacetophenone yielded 4-tolyl β-(4-phenylanilino)-β-4-tolylethyl ketone (IX). Condensation of 4-tolyl-4-aminobiphenyl with 4-methoxyacetophenone yielded 4-anisyl β-(4-phenylanilino)-β-4-tolylethyl ketone (X). Condensation of 4-tolyl-4-aminobiphenyl with 4-chloroacetophenone yielded 4-chlorophenyl β-(4-phenylanilino)-β-4-tolylethyl ketone (XI). Condensation of 4-tolyl-4-aminobiphenyl with 4-bromoacetophenone yielded 4-bromophenyl β-(4-phenylanilino-β-4-tolylethyl ketone (XII).

TABLE 1

Sample No.	Compound	M. p., °C	Yield, %	N, % found	N, % calc.
I		183 — 184	47,0	3,91 3,91	3,71
II		136 — 137	20,0	3,29 3,30	3,58
III		186 — 187	15,0	3,60 3,60	3,44
IV		166 — 168	25,0	3,46 3,32	3,40
V		174 — 175	53,0	3,25 3,07	3,06
VI		217 — 218	35,0	3,11 3,32	3,09
VII		214 — 215	12,0	3,41 3,13	3,17
VIII		171—172,5	20,0	3,36 3,22	3,54
IX		153—154,5	18,0	3,55 3,70	3,45
X		176 — 177	23,0	3,12 3,12	3,32
XI		145 — 147	27,0	3,07 3,07	3,29
XII		145 — 146	37,0	2,88 2,73	2,97

All the compounds we synthesized were obtained for the first time. 4-Aminobiphenyl hydrochloride was used as a catalyst.

The mechanism of the reaction we studied may be represented by the equation:



Procedure. The procedure for synthesizing the β-arylamino ketones was as follows. A reaction mixture consisting of 0.05 mole of Schiff's base, 0.05 mole of aliphatic-aromatic ketone, 10-15 ml of alcohol, and 0.5-1.0 g of 4-aminobiphenyl hydrochloride was heated on a water bath for 15-30 min. When the mixture had cooled, the precipitate was collected, treated with aqueous ammonia, and recrystallized from a mixture of alcohol and benzene. The results we obtained and the constants of the compounds synthesized are presented in Table 1.

Thus, in the present work it was possible to develop a new and convenient method of synthesizing β-arylamino ketones containing a biphenyl nucleus.

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*Original Russian pagination. See C. B. translation.

PHOSPHORYLATED CHLOROVINYL KETONES:

PRIMARY PRODUCTS OF THE REACTION OF PHOSPHORUS PENTACHLORIDE WITH ENOLACETATES

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We previously [1] described the preparation of phosphorylated β-chlorovinyl ketones by the reaction of phosphorus pentachloride and enolacetates with heating.

Further study of this reaction made it possible to find conditions under which it could be stopped at the initial stage, i.e., at the addition of phosphorus pentachloride to the multiple bond of the unsaturated ester with two moles of PCl_5.

$$R-\underset{\underset{OCOCH_3}{|}}{C}=CH_2 + 2PCl_5 \xrightarrow{\text{low temp.}} R-\underset{\underset{OCOCH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2PCl_4PCl_5. \qquad (I)$$

The composition given for the addition product was confirmed by analysis on the example of vinyl acetate. Due to the ready hydrolyzability of these products by atmospheric moisture and their instability at room temperature, they were then treated (without isolation from the reaction mixture) with sulfur dioxide at low temperature. We thus obtained acid chlorides of β-acetoxy-β-chloroalkylphosphinic acids, which were found to be sufficiently stable to isolate in a pure form.

$$R-\underset{\underset{OCOCH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2-PCl_4PCl_5 \xrightarrow[\text{low temp.}]{SO_2} R-\underset{\underset{OCOCH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2-POCl_2 + POCl_3 + 2SOCl_2. \qquad (II)$$

The yields of the acid chlorides of β-acetoxy-β-chloroethyl- and β-acetoxy-β-chloropropylphosphinic acids were 85 and 70% respectively. When the ratio of enol acetate to phosphorus pentachloride was 1:1, the acid chloride yield did not exceed 40% in either case. This is further indirect evidence in favor of the composition inequation (I) for the product of addition to vinyl acetate and also, apparently, isopropenyl acetate.

It should be noted that the reaction conditions for vinyl acetate and isopropenyl acetate were somewhat different. In the first case the addition of phosphorus pentachloride had to be carried out at 7-8° and in the second case, at −25°, which is explained by the different stabilities of the addition products. Thus, raising the temperature by a few degrees (to +15 and −15°, respectively) led to the formation of a mixture of products from which it was impossible to isolate individual substances by distillation alone (after treatment with sulfur dioxide).

An analogous difference was observed in the stabilities of the acid chlorides obtained from the addition products. Thus, the acid chloride of β-acetoxy-β-chloroethylphosphinic acid distilled in vacuum without decomposition, while the acid chloride of β-acetoxy-β-chloropropylphosphinic acid lost acetyl chloride at a temperature above 95° to give an 83% yield of the crystalline acid chloride of acetonylphosphinic acid.

$$CH_3-C(Cl)(OCOCH_3)-CH_2POCl_2 \xrightarrow{\text{above } 95^\circ} CH_3COCH_2POCl_2 + CH_3COCl \qquad \text{(III)}$$

The action of alcohol in the presence of pyridine on the acid chloride of β-acetoxy-β-chloroethylphosphinic acid yielded the corresponding diethyl ester, which was hydrolyzed by water in a few hours with heating or in 3-4 days at room temperature to give phosphonacetaldehyde.

$$CH_3COOCH(Cl)-CH_2-PO(OC_2H_5)_2 + H_2O \rightarrow C(=O)(H)-CH_2PO(OC_2H_5)_2 + CH_3COOH + HCl \qquad \text{(IV)}$$

Attempts to prepare the diethyl ester of β-acetoxy-β-chloropropylphosphinic acid both in the presence of pyridine and without it were unsuccessful; only phosphonacetone could be isolated from the reaction products in both cases. Phosphonacetone was also obtained by the action of alcohol on the acid chloride of acetonylphosphinic acid in the presence of pyridine.

The formation of the acid chloride of acetonylphosphinic acid, like the formation of phosphonacetaldehyde, demonstrates the structure given above for the hydrocarbon radical of the addition products and also shows that the addition occurred in accordance with Markovnikov's rule.

EXPERIMENTAL

Preparation of the addition products of PCl_5 and vinyl acetate ($CH_3COOCH(Cl)-CH_2-PCl_4PCl_5$). With stirring and cooling to 7-8°, 8.6 g (0.1 mole) of vinyl acetate was added dropwise to a filtered solution of 41.6 g (0.2 mole) of phosphorus pentachloride in 250 ml of carbon tetrachloride. Stirring was continued for a further 6 hr (at the same temperature) and part of the precipitate collected in a glass filter, cooled externally with dry ice. The precipitate was washed twice with carbon tetrachloride, then isopentane, and analyzed immediately. (The isopentane residues were removed in vacuum and air was not sucked through the filter.)

Found %: C 9.22; 9.90; H 1.16; 1.65; P 12.25; 12.29. $C_4H_6O_2P_2Cl_{10}$. Calculated %: C 9.56; H 1.20; P 12.22.

Acid chloride of β-acetoxy-β-chloroethylphosphinic acid. The addition product was obtained as described above from 83.5 g (0.4 mole) of phosphorus pentachloride in 330 ml of carbon tetrachloride and 17.7 g (0.2 mole) of vinyl acetate. Then, without isolation of the product, sulfur dioxide was passed through the reaction mixture at 5-7° until the precipitate dissolved completely. The carbon tetrachloride, thionyl chloride, and phosphorus oxychloride were then removed in the vacuum of a water pump and the residue vacuum distilled. We obtained 40.8 g (85% of theoretical) of the acid chloride of β-acetoxy-β-chloroethylphosphinic acid. It had b. p. 99-100°/1.5 mm; n_D^{20} 1.4855, d_4^{20} 1.5035; MR_D found 45.68, calculated 45.25.

Found %: C 20.02; 20.36; H 2.66; 2.78; P 12.72; 12.71; Cl 44.23; 44.27. $C_4H_6O_3PCl_3$. Calculated %: C 20.06; H 2.53; P 12.97; Cl 44.42.

Under analogous conditions, 41.6 g (0.2 mole) of phosphorus pentachloride and 17.2 g (0.2 mole) of vinyl acetate yielded 20.8 g (40% of theoretical) of the acid chloride of β-acetoxy-β-chloroethylphosphinic acid.

Acid chloride of acetonylphosphinic acid. Over a period of 20 min, 20 g (0.2 mole) of isopropenyl acetate was added dropwise with stirring and cooling to −24-26° to a filtered solution of 83.5 g (0.4 mole) of phosphorus pentachloride in 650 ml of carbon tetrachloride. After the reaction mixture had been stirred for 2 hr at the same temperature, sulfur dioxide was passed in (at −25°) until the precipitate dissolved completely. The solvent, thionyl chloride, and phosphorus oxychloride were removed in the vacuum of a water pump. When the residue

was vacuum distilled, decomposition of the substance was observed even at 60-70°. After complete decomposition, the residue was distilled at 89.5-90°/1.5 mm to give a colorless liquid which rapidly crystallized in the receiver. The yield of the acid chloride of acetonylphosphinic acid was 21 g (60% of theoretical) and the substance had m. p. 39-40°.

Found %: C 21.02; 20.68; H 3.03; 2.99; P 17.18; 17.27. $C_3H_5O_2PCl_2$. Calculated %: C 20.59; H 2.88; P 17.75.

Under analogous conditions, 83.5 g (0.4 mole) of phosphorus pentachloride and 40 g (0.4 mole) of isopropenyl acetate yielded 26 g (37% of theoretical) of the acid chloride of acetonylphosphinic acid.

Acid chloride of β-acetoxy-β-chloropropylphosphinic acid. Under the conditions of the previous experiment we prepared the addition product from 83.5 g of phosphorus pentachloride and 20 g of isopropenyl acetate. After sulfur dioxide had been passed through the reaction mixture (at −25°), the solvent, thionyl chloride, and phosphorus oxychloride were removed in a water-pump vacuum at 20-25°. The residue crystallized completely when cooled with ice. The yield of the unpurified product was 47 g (95% of theoretical). Recrystallization from dry isopentane yielded 35.5 g (70% of theoretical) of the acid chloride of β-acetoxy-β-chloropropylphosphinic acid in the form of colorless needles with m. p. 45.5-46.5°, which were slightly soluble in isopentane and readily soluble in the usual organic solvents.

Found %: C 23.98; 23.96; H 3.26; 3.41; P 12.37; 12.42. $C_5H_8O_3PCl$. Calculated %: C 23.67; H 3.18; P 12.21.

Conversion of the acid chloride of β-acetoxy-β-chloropropylphosphinic acid into the acid chloride of acetonylphosphinic acid. The acid chloride of β-acetoxy-β-chloropropylphosphinic acid (9.9 g) was heated on a bath at 95-105°. Acetyl chloride (2.7 g, 88% of theoretical) distilled; acetanilide from it had m. p. 114-115° and a mixed melting point with an authentic sample was not depressed. The residue was vacuum distilled at 92-93°/2 mm. We obtained 5.0 g (83.8% of theoretical) of the acid chloride of acetonylphosphinic acid as colorless platelets with m. p. 39-40°.

Diethyl β-acetoxy-β-chloroethylphosphinate. A mixture of 18.4 g (0.4 mole) of absolute ethyl alcohol, 31.6 g (0.4 mole) of pyridine, and 25 ml of ether was added dropwise with stirring and cooling to 0° to a solution of 47.9 g (0.2 mole) of the acid chloride of β-acetoxy-β-chloroethylphosphinic acid in 150 ml of absolute ether. The mixture was stirred for another hour while the temperature rose to room temperature, boiled for 1 hr, and filtered. The filtrate was concentrated and cooled to −10°. Colorless crystals with m. p. 62-63° precipitated. The precipitate, which consisted of pyridine hydrochloride and the phosphinic ester, was treated three times with boiling absolute ether and the ether extracts combined and concentrated. When cooled, the solution deposited coarse, colorless crystals with m. p. 64-65°. The total yield of diethyl β-acetoxy-β-chloroethylphosphinate was 41 g (79% of theoretical). When left in the open air, the crystals slowly (over 10 days) deliquesced with the liberation of acetyl chloride.

Found %: C 37.40; 37.18; H 6.42; 6.42; P 12.01; 11.99. $C_8H_{16}O_5PCl$. Calculated %: C 37.15; H 6.23; P 11.98.

Esterification of the acid chloride of β-acetoxy-β-chloropropylphosphinic acid. A. In the absence of base. Over a period of 20 min, 12.9 g of absolute ethyl alcohol was added dropwise with stirring, but without external cooling (no reaction occurred after one and a half hours at −3° and the original acid chloride was recovered) to a solution of 35.5 g of the acid chloride of β-acetoxy-β-chloropropylphosphinic acid (immediately after its preparation) in 160 ml of ether. The mixture was heated for half an hour at 30°, the ether and hydrogen chloride evaporated, and the residue vacuum-distilled. We obtained 16.3 g (60% of theoretical) of the diethyl ester of phosphonacetone with b. p. 101-102°/2.5 mm; n_D^{20} 1.4364, d_4^{20} 1.1117; MR_D found 45-73, calculated 45.40.

Literature data: b. p. 106-106.5/8.6 mm, n_D^{20} 1.4332, d_4^{20} 1.1127; b. p. 99-100°/1.5 mm, n_D^{20} 1.4355, d_4^{20} 1.1232 [2].

B. In the presence of pyridine. A mixture of 7.1 g of absolute ethyl alcohol and 12.1 g of pyridine was added dropwise with stirring and cooling to 0° to a solution of 19.4 g of the acid chloride of β-acetoxy-β-chloropropylphosphinic acid in 120 ml of ether. The mixture was then heated at 35-40° for 1 hr and the precipitate collected and washed with ether. After a day, the fresh precipitate was removed and the filtrate distilled to yield 6.8 g (47% of theoretical) of phosphonacetone with b. p. 122°/8 mm; n_D^{20} 1.4370; d_4^{20} 1.1129.

Esterification of the acid chloride of acetonylphosphinic acid. Over a period of an hour a solution of 17.6 g of the acid chloride of acetonylphosphinic acid in 40 ml of ether was added dropwise with stirring to a mixture of 10.2 g of absolute ethyl alcohol, 16.8 g of pyridine, and 60 ml of ether. The mixture was then boiled for an hour, the precipitate removed, the ether distilled from the filtrate, and the residue vacuum distilled. We obtained 14.1 g (76.6% of theoretical) of phosphonacetone with b. p. 94-95°/1 mm; n_D^{20} 1.4370, d_4^{20} 1.1131; MR_D found 45.70, calculated 45.40.

Found %: C 43.34; H 7.79; P 15.88. $C_7H_{15}O_4P$. Calculated %: C 43.30; H 7.79; P 15.96.

Preparation of phosphonacetaldehyde. A. In acetone acetone at room temperature. To a solution of 6 g of diethyl β-acetoxy-β-chloroethylphosphinate in 10 ml of acetone was added 1 g of water and the mixture left at room temperature. After 4 days the acetone and acetic acid were removed by distillation and the residue vacuum-distilled. We obtained 2.8 g (66.6% of theoretical) of the diethyl ester of phosphonacetaldehyde with b. p. 92-93°/2 mm; n_D^{20} 1.4383, d_4^{20} 1.1476; MR_D found 41.23, calculated 40.79.

B. In dioxane with heating. To a solution of 9 g of diethyl β-acetoxy-β-chloroethylphosphinate in 25 ml of dioxane was added 1.2 g of water and the mixture heated at 55-65° for 5 hr. The dioxane and acetic acid were removed by distillation and the residue vacuum-distilled. We obtained 4.1 g (67% of theoretical) of phosphonacetaldehyde with b. p. 92-93°/2 mm; n_D^{20} 1.4382; d_4^{20} 1.1473; MR_D found 41.23, calculated 40.79.

Found %: C 39.92; 39.96; H 7.27; 7.34; P 17.02; 17.01. $C_6H_{13}O_4P$. Calculated %: C 40.01; H 7.27; P 17.20.

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*Original Russian pagination. See C. B. translation.

ISOMERIZATION OF TETRANITROALKANES

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We recently showed that 1,1,1,3-tetranitropropane (I) is isomerized to symmetrical tetranitropropane (II) under the action of ammonia in alcohol [1].

$$\underset{\text{(I)}}{(NO_2)_3CCH_2CH_2NO_2} \rightarrow \underset{\text{(II)}}{(NO_2)_2CHCH_2CH(NO_2)_2}.$$

In the present work it was found that 1,1,1,3-tetranitropropane is isomerized to symmetrical tetranitropropane not only in the presence of ammonia, but also under the action of some other alkaline agents, namely, potassium acetate and potassium methylate. It should be emphasized that the nature of the solvent has a substantial effect on the course of the reaction. Thus, if the reaction of 1,1,1,3-tetranitropropane with potassium acetate was carried out in alcohol, isomerization occurred and 1,1,3,3-tetranitropropane was formed in 33.4% yield.* If a mixture of acetone and alcohol was used as solvent, no isomerization occurred and there was only elimination of a nitro group from the starting 1,1,1,3-tetranitropropane with the formation of 1,1,3-trinitropropane. 1,1,1,3-Tetranitropropane (I) was isomerized to symmetrical tetranitropropane (II) in 10.8% yield in the presence of potassium methylate (in methanol).

Wishing to determine whether the isomerization was specific for 1,1,1,3-tetranitropropane or whether it occurred with other compounds of similar structure, we studied the action of bases on 1,1,1,3-tetranitrobutane and 1,1,1,3-tetranitropentane. The study of these compounds was of additional interest as, unlike 1,1,1,3-tetranitropropane, they exist as two stable forms, namely, the true and the aci forms [2]. A comparative study of the isomerization of these two forms could shed light on the mechanism of the reaction

$$(NO_2)_3CCH_2\underset{\underset{R}{|}}{C}=NO_2H \rightleftarrows (NO_2)_3CCH_2\underset{\underset{R}{|}}{C}HNO_2,$$

(IIIa) R = CH_3; (IVa) R = C_2H_5 (IIIb) R = CH_3; (IVb) R = C_2H_5.

It was found that the aci form of tetranitrobutane (IIIa) was readily isomerized to 1,1,3,3-tetranitrobutane (V) under the action of potassium acetate in alcohol (34.5% yield), potassium methylate in methanol (36.7% yield), and also an alcohol solution of potassium hydroxide (12.1% yield). The isomerization could also be accomplished in the presence of dimethylamine, but under these conditions the reaction product yield did not exceed a few percent.

The true form of 1,1,1,3-tetranitrobutane (IIIb) was also isomerized to 1,1,3,3-tetranitrobutane (V) under the action of potassium acetate (34.5% yield) and potassium hydroxide in alcohol (12.8% yield), but, in contrast

*Here and later the yield was calculated on the potassium salts of the corresponding nitroalkanes.

to the aci form, it was not isomerized in the presence of potassium methylate.

The aci form of 1,1,1,3-tetranitropentane (IVa), like 1,1,1,3-tetranitropropane and 1,1,1,3-tetranitrobutane, also underwent isomerization, but the process only occurred in the presence of potassium acetate. The yield of isomerization product, namely, 1,1,3,3-tetranitropentane (VI), was 14.5%. The isomerization did not occur in the presence of other alkaline agents.

$$(NO_2)_3CCH_2\underset{\underset{R}{|}}{C} = NO_2H \rightarrow (NO_2)_2CHCH_2\underset{\underset{R}{|}}{C}(NO_2)_2$$

(IIIa) R = CH_3; (IVa) R = C_2H_5 (V) R = CH_3; (VI) R = C_2H_5.

Finally, the true form of 1,1,1,3-tetranitropentane (IVb) was not isomerized at all in the presence of alkaline agents.

It should be noted that 1,1,1,3-tetranitrobutane and 1,1,1,3-tetranitropentane (both aci and true forms) were not isomerized in the presence of ammonia, in contrast to 1,1,1,3-tetranitropropane.

On comparing the results of studying the aci and true forms of 1,1,1,3-tetranitrobutane and 1,1,1,3-tetranitropentane it is readily seen that the aci forms were isomerized more readily than the corresponding true forms. On the basis of this it may be considered that the isomerization of 1,1,1,3-tetranitroalkanes proceeds through the formation of the aci form:

$$(NO_2)_3CCH_2\underset{\underset{R}{|}}{C}HNO_2 \rightarrow (NO_2)_3CCH_2\underset{\underset{R}{|}}{C} = NO_2H \rightarrow (NO_2)_2CHCH_2\underset{\underset{R}{|}}{C}(NO_2)_2$$

R = H, CH_3, C_2H_5

The isomerization products, 1,1,3,3-tetranitroalkanes (II), (V), and (VI), were isolated as their potassium salts, which were analyzed for potassium.

By treatment with bromine, the potassium salts were converted into the corresponding bromides, namely, 1,3-dibromo-1,1,3,3-tetranitropropane, 1-bromo-1,1,3,3-tetranitrobutane, and 1-bromo-1,1,3,3-tetranitropentane.

On the basis of the results obtained in the present work, we may draw the conclusion that isomerization with transfer of a nitro group is a general reaction for 1,1,1,3-tetranitroalkanes with a straight chain of carbon atoms.

EXPERIMENTAL

Isomerization of 1,1,1,3-tetranitropropane (I) to 1,1,3,3-tetranitropropane (II).

a) In the presence of potassium acetate. A solution of 4.9 g (0.05 mole) of fused potassium acetate in 25 ml of alcohol, kept at 0°, was added dropwise with stirring to a solution of 5.6 g (0.025 mole) of 1,1,1,3-tetranitropropane in 35 ml of alcohol, cooled in ice. After the potassium acetate had been added, the solution was stirred at 0° for 2.5 hr and at room temperature for 1 hr. The precipitate was collected, washed with a small amount of ice water, then acetone, and finally a small amount of dry ether, and dried in air. We obtained 2.5 g (33.4%) of the dipotassium salt of 1,1,3,3-tetranitropropane. The m. p. was 221° (with decomp.) (after recrystallization from water).

Found %: K 26.41; 26.22. $C_3H_2N_4O_8K_2$. Calculated %: K 26.03.

b) In the presence of potassium methylate. With stirring and cooling in ice, 40 ml of a 1 N solution of potassium methylate (0.04 mole), kept at no higher than 0°, was added dropwise to a solution of 4.5 g (0.02 mole) of 1,1,1,3-tetranitropropane in 15 ml of absolute methanol. When the potassium methylate had been added, the mixture was stirred at 0° for 1 hr and at 10° for 1 hr. The precipitate was collected and washed repeatedly with acetone. The residue was washed with a small amount of dry ether and dried in air. We obtained 0.65 g (10.8%) of the dipotassium salt of 1,1,3,3-tetranitropropane.

Found %: K 26.26; 26.17; $C_3H_2N_4O_8K_2$. Calculated %: K 26.03.

From this salt we prepared 1,3-dibromo-1,1,3,3-tetranitropropane [1].

Isomerization of the aci form of 1,1,1,3-tetranitrobutane (IIIa) to 1,1,3,3-tetranitrobutane (V).

a) In the presence of potassium acetate. The aci form of 1,1,1,3-tetranitrobutane (4 g, 0.0168 mole) was dissolved in 24 ml of alcohol at 0°. A solution of 1.7 g (0.0174 mole) of fused potassium acetate in 20 ml of alcohol, kept at 6-8°, was added dropwise with stirring and cooling with ice to the solution obtained. The mixture was stirred at room temperature for 4 hr. The solution was decanted, a small amount of ice water added to the residual precipitate, and the crystalline reaction product collected, washed with a small amount of cold alcohol and ether, and dried in air. We obtained 1.6 g (34.5%) of the potassium salt of 1,1,3,3-tetranitrobutane. The m. p. was 118° (with decomp.) (after recrystallization from 50% methanol). Literature data: m. p. 137-138° [3].

Found %: K 14.09; 14.17. $C_4H_5N_4O_8K$. Calculated %: K 14.16.

b) In the presence of potassium methylate. With stirring and cooling in ice and salt, 1.8 g (0.0075 mole) of the aci form of 1,1,1,3-tetranitrobutane, kept at below −5°, was added in several portions to 7.5 ml of 1 N potassium methylate solution (0.0075 mole) and 3 ml of absolute methanol. The mixture was then stirred at −10° for 45 min and the precipitate collected, washed with small amounts of ice water, cold alcohol, and dry ether, dried in air, and recrystallized from 50% methanol. We obtained 0.75 g (36.7%) of the potassium salt of 1,1,3,3-tetranitrobutane.*

c) In the presence of potassium hydroxide. The aci form of 1,1,1,3-tetranitrobutane (2.5 g, 0.0105 mole) was dissolved in 10 ml of alcohol at 0°. A solution of 0.6 g (0.0107 mole) of potassium hydroxide in 10 ml of alcohol, kept at no higher than 10°, was added with stirring and cooling in ice to the solution obtained. The mixture was then stirred at room temperature for 3.5 hr, the solution decanted, a small amount of ice water added to the residual precipitate, the crystalline reaction product collected, washed with a small amount of cold alcohol and ether, and dried in air. We obtained 0.35 g (12.1%) of the potassium salt of 1,1,3,3-tetranitrobutane.

1-Bromo-1,1,3,3-tetranitrobutane. The calculated amount of bromine was added with stirring and cooling with ice to 2.6 g (0.0094 mole) of the potassium salt of 1,1,3,3-tetranitrobutane, covered with a layer of ether. The ether solution was filtered and dried with calcium chloride. Removal of the ether yielded 3 g (100%) of crystalline 1-bromo-1,1,3,3-tetranitrobutane. The m. p. was 46° (after recrystallization from hexane at 40° with subsequent freezing).

Found %: Br 25.13; 25.26. $C_4H_5N_4O_8Br$. Calculated %: Br 25.22.

Isomerization of true form of 1,1,1,3-tetranitrobutane (IIIb) to 1,1,3,3-tetranitrobutane (V).

a) In the presence of potassium acetate. A solution of 1.65 g (0.0168 mole) of fused potassium acetate in 18 ml of alcohol kept at 15-18° was added dropwise with stirring and cooling with cold water to a solution 4 g (0.0168 mole) of the true form of 1,1,1,3-tetranitrobutane in 32 ml of alcohol. The mixture was stirred at room temperature for 4.5 hr and the precipitate collected, washed with a small amount of ice water, cold alcohol, and ether, and dried in air. We obtained 1.6 g (34.5%) of the potassium salt of 1,1,3,3-tetranitrobutane.

b) In the presence of potassium hydroxide. A solution of 0.25 g (0.0045 mole) of potassium hydroxide in 4 ml of alcohol at no higher than 10°, was added with stirring and cooling in ice water to a solution of 1 g (0.0042 mole) of the true form of 1,1,1,3-tetranitrobutane in 8 ml of alcohol. The mixture was stirred at room temperature for 3 hr and then left for 3 days. The solution was decanted, a small amount of ice water added to the residual precipitate, and the crystalline reaction product collected, washed with cold alcohol and ether, and dried in air. We obtained 0.15 g (12.8%) of the potassium salt of 1,1,3,3-tetranitrobutane.

Isomerization of the aci form of 1,1,1,3-tetranitropentane (IVa) to 1,1,3,3-tetranitropentane (VI). The aci form of 1,1,1,3 tetranitropentane (3 g, 0.012 mole) was dissolved in 12 ml of alcohol at 0°. A solution of 1.2 g (0.0123 mole) of fused potassium acetate in 12 ml of alcohol was added dropwise with stirring and cooling in

*In this and subsequent experiments the potassium salt of 1,1,3,3-tetranitrobutane was analyzed for potassium and also identified by the melting point. These data are not given to avoid repetition.

ice water to the solution obtained. When the potassium acetate had been added, the mixture was stirred at 0° for 2 hr and at room temperature for 3 hr and then left for 5 days. The precipitate was collected, washed with small amounts of ice water, cold alcohol, and ether, and dried in air. We obtained 0.5 g (14.5%) of the potassium salt of 1,1,3,3-tetranitropentane. The m. p. was 135° (with decomp.) (after recrystallization from 50% methanol).

Found %: K 13.15; 13.35. $C_5H_7N_4O_8K$. Calculated %: K 13.47.

1-Bromo-1,1,3,3-tetranitropentane. The calculated amount of bromine was added with stirring and cooling in ice water to 1.1 g (0.0038 mole) of the potassium salt of 1,1,3,3-tetranitropentane, covered with ether. The ether solution was filtered and dried with calcium chloride. Removal of the ether yielded 1.1 g (88%) of liquid 1-bromo-1,1,3,3-tetranitropentane with n_D^{20} 1.5060 (purified by solution in hexane with subsequent freezing).

Found %: Br 24.16; 24.02. $C_5H_7N_4O_8Br$. Calculated %: Br 24.14.

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SELECTIVITY OF AN ADSORBENT PRODUCED IN THE PRESENCE OF BACTERIA WITH RESPECT TO OPTICAL ISOMERS

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The separation of racemates by adsorption methods is of considerable theoretical and practical interest. Methods are known for the separation of racemates by selective solution of antipodes in an optically active solvent (or a film of an optically active compound deposited on an adsorbent). In this case the separation is based on the formation of labile diastereoisomers and the separation of the latter may be accomplished on normal adsorbents [1]. There are a large number of natural stereospecific adsorbents, which are capable of partial (or complete) separation of racemates. Among these adsorbents are the compounds of comparatively complex structure, proteins, and carbohydrates. It is possible to separate racemates on optically active quartz. However, the general rules of the separation of racemates on such adsorbents have not been found yet. Therefore, in recent years attention has been directed toward synthetic adsorbents with a given separatory adsorptive capacity.

In the work of M. V. Polyakov et al., [2], a method was proposed for the first time for preparing adsorbents, silica gels, which showed selective adsorption for the component in whose presence the gel had been formed. Selective adsorption of silica gel for benzene, toluene, and xylene was found. Later Dickey and other authors [3, 4] demonstrated that silica gel shows similar adsorption for a series of dyes. The selectivity of the adsorption was explained [2] by the formation of "impressions" of the molecules of the model on the adsorbent surface.

However, these authors did not extent the method to the preparation of optically selective adsorbents. The first such adsorbent was prepared by Curti and Colombo [5]. On silica gel formed in the presence of (+)-camphorsulfonic acid it was possible to obtain a 10% separation of mandelic acid and 30% separation of racemic camphorsulfonic acid. Grubhoffer and Schleith [6] increased the efficiency of the adsorbents by using an ion-exchange resin in which the carboxyl groups were esterified with quinine. A resin containing 35% of quinine acquired the capacity to separate almost completely racemic mandelic acid. Silica gel produced in the presence of quinine or quinidine was used to establish the configuration of compounds related to quinine or quinidine [7].

We prepared an optically selective adsorbent from silica gel formed in the presence of dissymmetric cultures of Bac. mycoides. The possibility of preparing such an optically selective adsorbent was based on the following considerations.

The soil bacteria, Bac. mycoides, are extremely widespread microorganisms, which are encountered in almost all soils (up to 225 thousand per gram of soil). The general appearance of their cultures grown in vessels with a nutrient medium is reminiscent of a spiral nebula with counterclockwise protuberances (left form) Almost all soils in USSR territory are populated by this left form, with the exception of a few regions where relic fauna and flora of the Tertiary period are retained. There, the right, inverse form of the bacteria predominate. The hypothesis has been put forward that the macrodissymmetry of the form of the colonies is caused by the dissymmetry of receptors present in the protoplasm, which are extremely sensitive to the action of optically active poisons. It is found that (−)-atabrine has a greater action than (+)-atabrine on the left form of Bac. mycoides.

while (+)-atabrine is more poisonous to the inverse, right form [7]. A difference in the development of right and left colonies has also been observed in the presence of optical isomers of other compounds. One might expect the appearance of dissymmetric receptors also in adsorption by the creation of "impressions" on the surface of an adsorbent.

The adsorbents were prepared by the following procedure which we developed. Two portions of acid silica gel were washed until neutral, the water decanted, and the gel covered with a standard meat peptone broth. The two gel samples were then inoculated with a right and left culture of Bac. mycoides. When the maximum growth of the cultures had been reached (10 days at 28°), the nutrient medium was decanted and the silica gel dried first in vacuum and then at 120° for 6 hr. The organic residues were removed by heating the silica gel with Perhydrol on a water bath until the evolution of oxygen ceased. The silica gel was then washed with water and dried at 120-150° for 2 hr. For comparison of the adsorption, a control sample of silica gel (specific surface according to the Brunauer, Emmett, and Teller method for benzene was 220 m^2/g and the effective pore radius by Kelvin's method, 80 A) was prepared under the same conditions, but in the absence of bacteria.

The optical selectivity of the adsorption of the three samples prepared was measured as the amount of adsorbed optical isomers of linalool. We used (−)-linalool with b. p. 90-91°/15 mm, d_4^{20} 0.8679; n_D^{20} 1.4634; $[\alpha]_D^{20} = -18.14°$ (93.6% optical purity) and (+)-linalool with b. p. 90-92°/15 mm, d_4^{20} 0.8660; n_D^{20} 1.4650; $[\alpha]_D^{20} = +13.5°$ (70.3% optical purity).

The adsorption was measured on a vacuum apparatus by a gravimetric method (accuracy of $1 \cdot 10^{-5}$ g) with the aid of McBain quartz spring balances at 20°. After the samples had undergone prolonged aging at 120° for 8 hr in vacuum, the adsorption of one linalool isomer was measured and then the adsorption of the other optical isomer was measured on fresh samples. Table 1 gives data on adsorption on the three silica gel samples investigated.

TABLE 1

Adsorbent	Adsorption in mmole/g of adsorbent		Ratio of mmoles adsorbed	
	(−)-linalool	(+)-linalool	$\frac{(-)\text{-linalool}}{(+)\text{-linalool}}$	$\frac{(+)\text{-linalool}}{(-)\text{-linalool}}$
Control silica gel	0.91	1.14	0.80	1.24
Silica gel produced with the right, inverse culture of Bac. mycoides	0.145	0.74	0.195	5.12
Silica gel produced with the left colony of Bac. mycoides	1.659	0.208	8.0	0.125

The vapor pressure of linalool is low (1 mm at 40°) and therefore the adsorption isotherm could not be constructed. Table 1 gives the number of millimoles of the alcohol adsorbed at saturation. The sample was considered saturated when there was no further increase in weight over 2.5 hr.

The data obtained show an essential difference in the adsorption of the two silica gel samples, which differed considerably from the adsorption of the control sample. Silica gel produced in the presence of the right, inverse colony of Bac. mycoides adsorbed 5.12 times more (+)-linalool than its isomer. Silica gel produced in the presence of the left form of Bac. mycoides adsorbed 8 times more (−)-linalool than (+)-linalool. The slight difference in the adsorption of (+)-and (−)-linalool on the control silica gel sample is explained by possible impurities in the original linalool. (−)-Linalool was adsorbed 11.4 times better on the "left" silica gel than on the "right," and (+)-linalool was adsorbed 3.6 times better on the right silica gel than on the left. If the selectivities of the adsorbents obtained (i. e., the degree of preferential adsorption of one optical isomer) are compared, then the ratios of the selectivities of the left silica gel to the right and the right to the left are identical and equal 41.

Apart from having a certain preparative value, the method proposed for preparing a stereospecific adsorbent is of interest for understanding the relation between molecular dissymmetry and the dissymmetry of the colony as this indirect method confirms the optically selective behavior of dissymmetric receptors of dissymmetric organisms. No direct demonstration of this has been given up to now; an attempt to use a polarimetric method to demonstrate a difference in the optical activity of the amino acid constituents of left and right forms of Aplexa hypnorum, Fruticicola lantzi Lindh., etc., were unsuccessful [8]. We are continuing experiments to elucidate the role of the nutrient medium in the formation of the specific surface of the silica gel.

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FERROCENESULFINIC ACIDS

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We previously described [1] the preparation of a sulfinic acid by reduction of ferrocenesulfonyl chloride with zinc dust. In the present work we synthesized ferrocenedisulfinic acid and studied the properties of the two acids.

Ferrocenedisulfinic acid was obtained by reduction of ferrocenedisulfonyl dichloride with zinc dust. It was difficultly soluble in water and organic solvents and solutions of it rapidly decomposed. The disodium salt of ferrocenedisulfinic acid was much more stable.

The ferrocenesulfinic acids, both mono- and diacids, reacted with mercuric chloride like benzenesulfinic acid to give mono- and di-(chloromercuri)-ferrocenes in high yield.

$$C_5H_5FeC_5H_4SO_2Na \xrightarrow{HgCl_2} C_5H_5FeC_5H_4HgCl,$$

$$Fe(C_5H_4SO_2Na)_2 \xrightarrow{HgCl_2} Fe(C_5H_4HgCl)_2.$$

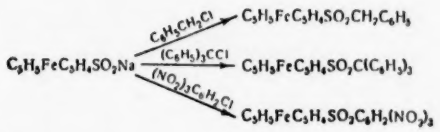
We attempted to prepare ferrocene derivatives of tin similarly by the action of stannous chloride on the sodium salt of the sulfinic acid, but it was found that reduction occurred and tin dithioferrocenolate was formed.

$$2C_5H_5FeC_5H_4SO_2Na \xrightarrow{SnCl_2} (C_5H_5FeC_5H_4S)_2Sn.$$

Tin thioferrocenolate was identified by conversion into thioferrocenyl benzoate.

We then used ferrocenemonosulfinic acid for the synthesis of ferrocenyl sulfones.

We previously [2] prepared phenyl ferrocenyl sulfone and differocenyl sulfone by the action of the acid halides of the corresponding sulfo acids on differocenylmercury. In the present work we synthesized benzyl, triphenylmethyl, and picryl ferrocenyl sulfones by reaction of sodium ferrocenemonosulfinate with benzyl chloride, triphenylmethyl chloride, and picryl chloride, respectively.



The yields were high (80-88% of theoretical).

Ferrocenyl ferrocenylmethyl sulfone was obtained in high yield by heating an aqueous solution of sodium ferrocenesulfinate with N,N-dimethylaminomethylferrocene iodomethylate.

EXPERIMENTAL

Reaction of sodium ferrocenesulfinate with mercuric chloride. To an aqueous solution of 0.31 g (0.001 mole) of sodium ferrocenesulfinate was added an alcohol solution of 0.27 g (0.001 mole) of mercuric chloride. A precipitate of chloromercuriferrocene [3] formed immediately and this was collected and dried. The weight was 0.41 g. The yield was quantitative. The m. p. and the m. p. of a mixture with chloromercuriferrocene were 194-196°.

Tin thioferrocenolate. To a suspension of 0.37 g (0.0012 mole) of the sodium salt of the sulfinic acid in alcohol was added 0.5 g of stannous chloride. When the light yellow precipitate which formed in the cold was heated it was converted into a red, crystalline substance, tin thioferrocenolate. The weight was 0.2 g (74% of theoretical). Tin thioferrocenolate was readily soluble in benzene, less so in ether, and insolbule in ligroin and n-heptane; it was purified by precipitation from benzene solution with ligroin.

Found %: C 43.68; 43.59; H 3.34; 3.37. $C_{20}H_{18}FeS_2Sn$. Calculated %: C 43.42; H 3.25.

The action of hydrochloric acid on tin thioferrocenolate gave ferrocenyl mercaptan, which was isolated as the benzoyl derivative. The m. p. and the m. p. of a mixture with an authentic sample were 138-139°.

Triphenylmethyl ferrocenyl sulfone. An ether suspension of 0.55 g (0.0018 mole) of sodium ferrocenesulfinate and 0.5 g (0.0018 mole) of triphenylmethyl chloride was heated for 4 hr. The precipitate of triphenylmethyl ferrocenyl sulfone was recrystallized from n-butyl alcohol. Triphenylmethyl ferrocenyl sulfone was a yellow crystalline substance, which was difficultly soluble in organic solvents and melted with decomposition at 220-221°.

Found %. C 70.09; 70.14; H 5.07; 5.04; S 6.35; 6.24; Fe 11.54; 11.32. $C_{29}H_{24}FeO_2S$. Calculated %: C 70.61; H 4.91; S 6.48; Fe 11.38.

Benzyl ferrocenyl sulfone. An alcohol solution of 0.55 g (0.0018 mole) of sodium ferrocenesulfinate and 0.5 g of benzyl chloride was boiled for 4 hr. The solvent was then removed by distillation and the residue extracted with benzene. The benzene extracts were chromatographed on an alumina column. The benzyl ferrocenyl sulfone was eluted with benzene. After recrystallization from alcohol, the product had m. p. 144-146°. The yield was 0.4 g (80% of theoretical).

Found %: C 59.88; 60.01; H 4.87; 4.84; Fe 16.20; 15.98. $C_{17}H_{16}FeO_2S$. Calculated %: C 60.01; H 4.73; Fe 16.46.

Picryl ferrocenyl sulfone. A mixture of 0.55 g (0.0018 mole) of sodium ferrocenesulfinate and 0.87 g (0.0035 mole) of picryl chloride was heated in alcohol for an hour. The picryl ferrocenyl sulfone, which formed a dark violet, crystalline precipitate, was purified by three reprecipitations from benzene with n-heptane and contained 0.5 molecules of benzene of crystallization. Picryl ferrocenyl sulfone was readily soluble in benzene, difficultly so in ethyl and butyl alcohols, and insoluble in ether and ligroin; it did not melt, but exploded on ignition. The yield was 88% of theoretical.

Found %: C 45.37; 45.39; H 2.87; 3.15; S 6.37; 6.17; Fe 11.46; 11.68. $C_{19}H_{14}FeO_8SN_3$. Calculated %: C 45.59; H 2.82; S 6.41; Fe 11.16.

Ferrocenyl ferrocenylmethyl sulfone.* A solution of 1.4 g (0.0036 mole) of N,N-dimethylaminomethylferrocene iodomethylate [4] in 150 ml of water was added to a solution of 1 g (0.0032 mole) of sodium ferrocenesulfinate in 70 ml of water . The mixture was heated for 3 hr at 80-90° and then boiled for 2 hr. The yellow precipitate of the sulfone was collected, washed carefully with water, and dried in a vacuum desiccator. The

*Ferrocenyl ferrocenylmethyl sulfone was prepared with the help of L. S. Shilovtseva and A. A. Ponomarenko.

weight was 1.35 g. Acidification of the filtrate with concentrated HCl yielded a further 0.15 g of sulfone. The total yield was 1.5 g (92% of theoretical). The decomposition point was above 175-180° (after reprecipitation from benzene solution with n-heptane).

Found %: C 55.98; 56.19; H 4.55; 4.41; Fe 24.36; 24.25; S 6.95; 7.18. $C_{21}H_{20}FeSO_2$. Calculated %: C 56.30; H 4.47; Fe 24.94; S 7.40.

Ferrocenedisulfonyl dichloride.* The complex of ferrocenedisulfonic acid with dioxane [5] (32 g, 0.074 mole) was added in small portions to 100 ml of $POCl_3$. The mixture was heated on a water bath for 40 min and then cooled and poured onto ice. The precipitate was collected and extracted several times with hot dichloroethane. The solution of the disulfonyl dichloride in dichloroethane was dried with magnesium sulfate. The dichloroethane was evaporated until crystallization began. The ferrocenedisulfonyl dichloride which precipitated when the solution was cooled to 0° was collected and washed with dichloroethane. The weight was 15 g. A further 2 g of diacid chloride was isolated from the mother liquor. The total yield was 17 g (60% of theoretical). Ferrocenedisulfonyl dichloride was recrystallized from a mixture (1 : 1) of dichloroethane and CCl_4; when heated above 150° it decomposed vigorously.

Ferrocenedisulfinic acid and its sodium salt. A saturated benzene solution of 6 g (0.0145 mole) of ferrocenedisulfonyl dichloride was heated with 10 g of zinc dust and 1 ml of water for 3-4 hr (until the benzene solution was completely decolorized). During the heating, fresh portions of zinc dust (2 g each) and water (0.5 ml each) were added three times. The precipitate was then collected and heated with 4 portions (150 ml each) of soda solution, saturated in the cold. The soda solution was carefully acidified with concentrated HCl with cooling in ice water to avoid decomposition of the ferrocenedisulfinic acid. A flocculent precipitate of ferrocenedisulfinic acid formed. The weight was 2.75 g. The yield was 56% of theoretical.** Ferrocenedisulfinic acid was a yellow, powdery substance with decomp. p. 126-128°, which was difficultly soluble in water and organic solvents. When solutions of it were heated, rapid decomposition occurred. The sodium salt of ferrocenedisulfinic acid was obtained by precipitation with 40% alkali from alcohol or weakly alkaline aqueous solutions and also directly from a soda solution of the sodium salt. After recrystallization from alcohol, the sodium salt of the disulfinic acid was a yellow crystalline substance, which was readily soluble in water and methyl and ethyl alcohols; when heated, it decomposed without melting at 290-298°; it contained three molecules of water of crystallization.

Found %: C 28.97; 28.90; H 3.75; 3.64; S 14.82; 14.92. $C_{10}H_{14}FeO_7S_2Na_2$. Calculated %: C 29.1; H 3.42; S 15.35.

Reaction of sodium ferrocenedisulfinate with mercuric chloride. Heating 0.32 g (0.0078 mole) of an alcohol solution of sodium ferrocenedisulfinate and 0.55 g (0.002 mole) of mercuric chloride formed di-(chloromercuri)-ferrocene [3] (separated as a yellow precipitate). The yield was 0.41 g (80% of theoretical).

Found %: C 18.64; 18.57; H 1.49; 1.36. $C_{10}H_8FeHg_2Cl_2$. Calculated %: C 18.32; H 1.23.

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*We previously [1] described the preparation of ferrocenedisulfonyl dichloride from the lead salt of the disulfonic acid. In the present work we found that the diacid chloride was obtained readily from the complex of ferrocenedisulfonic acid with dioxane, which made the preparation of the lead salt unnecessary.

**There was some complication in the preparation of ferrocenedisulfinic acid that we could not explain as we were sometimes unable to isolate it by acidification of the soda solution with concentrated HCl, despite careful observation of the conditions of successful experiments.

***Original Russian pagination. See C. B. translation.

INVESTIGATION OF THE CRYSTALLIZATION POINT OF BICYCLO-(2,2,1)-HEPTADIENE-2,5 AND CYCLOHEPTATRIENE AND MIXTURES OF THEM

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Original article submitted January 12, 1960

We recently [1] described the synthesis and some of the physical properties of bicyclo-(2,2,1)-heptadiene-2,5 (I), the starting material for the production of the insecticide Aldrin, and its isomerization product, cycloheptatriene (II).

(I)

(II)

The parameter which is most sensitive to the presence of foreign substances and which is most convenient for determining the degree of purity of a preparation is the crystallization point. Therefore, in the present work we determined the crystallization points, cryoscopic constants, and degrees of purity of hydrocarbons (I) and (II). We also studied the melting point diagram of the system bicycloheptadiene–cycloheptatriene. The cryoscopic method which we used has been published previously [2].

TABLE 1

Hydrocarbon	B. p., °C	n_D^{20}	d_4^{20}	Crystallization point, °C		Cryoscopic constant, mole fraction per °C	Purity of preparation, mol. %
				starting substance	absolutely pure substance		
Bicyclo-(2,2,1)-heptadiene-2,5	90.3	1.4702	0.9064	−19.1	−18.9	0.007	99.86
Cycloheptatriene	115.6	1.5244	0.8915	−75.1	−74.8	0.005	99.85

The hydrocarbons were first purified by two distillations on a column with an efficiency of 50 theoretical plates with a glass packing. For the investigation we took several of the intermediate fractions from the distillation, which lay on the plateau and had identical boiling points, refractive indices, and specific gravities. This made it possible to establish which of the fractions was most pure. The amount of impurities was determined from the depression of the crystallization point. Each experiment required 1.5-2 ml of substance. The crystal-

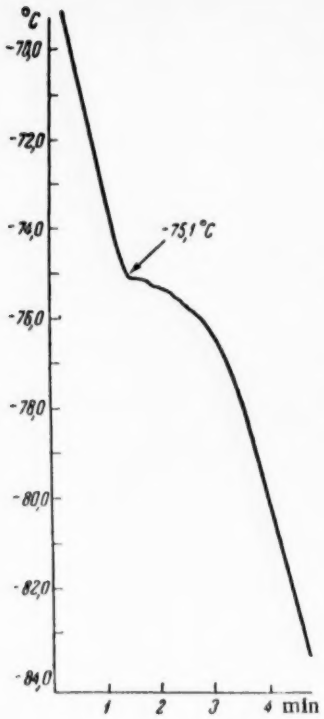

Fig. 1. Crystallization curve of cycloheptatriene.

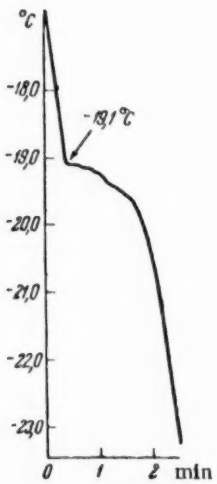

Fig. 2. Crystallization curve of bicycloheptadiene.

lization point was measured with an accuracy of up to ±0.05°C. The data obtained and also other constants of the substances investigated are given in Table 1.

Figures 1 and 2 show crystallization curves of the starting preparations. Available literature data on the crystallization point of bicycloheptadiene are approxmiate (~−25°) [3]. Therefore, we will not discuss them. The crystallization point of cycloheptatriene was determined by Kohler [4] and Finke [5]. The data of Kohler (−79.49°) differ considerable from ours. What is at first glance a large discrepancy in crystallization points when the boiling points and refractive indices are similar (b. p. 115.50°, n_D^{20} 1.5243) is quite natural in principle as cycloheptatriene has a low cryoscopic constant of 0.005 (the dimensions of the cryoscopic constant are mole fractions per degree centigrade). This means that even very small amounts of impurity lead to appreciable depression of the crystallization point. *

According to our calculations the preparation of Kohler contained about 2.3% of impurity, which is extremely probable as the substance changes very readily. It should be noted that in the determination of the crystallization point of cycloheptatriene the substance should be carefully protected from air for if the preparation remains open to the air for even a short time (1 hr), the crystallization point is depressed. Later Finke [5] obtained a crystallization point for cycloheptatriene which agrees with ours (−75.24°). The cryoscopic constant he reported (0.003564) is also close to ours.

The cryoscopic constants of the substances, which were necessary for determining the purity, we determined by measuring the depression in crystallization point from a definite amount of artificially introduced impurity. To (I) and (II) we added various amounts (from 0.5 to 2%) of toluene and n-heptane. In all cases, the results obtained for the same substance coincided. We then attempted to contaminate (I) and (II) with each other. They could be obtained from the same synthesis. This gives the probability of mutual contamination when the substances were not purified sufficiently (this probability is decreased by careful purification as their parameters are quite different as can be seen from Table 1).

We carried out experiments in which various amounts of (I) were added to (II) and vice versa and observed proportionality between the change in crystallization point and the amount of artificial impurity. When bicycloheptadiene was contaminated with cycloheptatriene, the normal picture of depression of crystallization point by impurities was observed. When there was a small amount of impurity, the crystallization point was depressed in proportion to the amount of impurity added in accordance with the laws of ideal and dilute solutions (Table 2).

The cryoscopic constant calculated from these data coincided with the value obtained for this substance when the artificial impurity was toluene or n-heptane.

When bicycloheptadiene was the impurity in cycloheptatriene a slight depression of crystallization point was observed only when 0.2, 0.4, and 0.8% of bicycloheptadiene was added. When the impurity concentration was only slightly more than 1%, the crystallization point of the mixture was found to be even higher than the crystallization point of the pure substance (see Table 2, No. 5 etc., and Fig. 3).

*In particular, this explains the high slope of the plateaus of the crystallization curves of cycloheptatriene and bicycloheptadiene shown in Figs. 1 and 2.

TABLE 2

Sample No.	Comp. of mixture investigated, %		Crystallization point, °C	Difference between crystallization points of mixture and cycloheptatriene, °C
	bicycloheptadiene	cycloheptatriene		
1	—	100,00	—75,07	—
2	0,21	99,79	—75,23	—0,16
3	0,44	99,56	—75,40	—0,33
4	0,80	99,20	—75,13	—0,06
5	1,67	98,33	—74,81	+0,26
6	3,38	96,62	—73,69	+1,38
7	7,26	92,74	—72,52	+2,55
8	20,01	79,99	—69,00	+6,07
9	57,84	42,16	—60,00	+15,07
10	84,77	15,23	—43,50	+31,57
11	95,42	4,58	—26,60	+48,47
12	97,73	2,27	—22,14	+52,93
13	98,81	1,19	—21,00	+54,07
14	100,00	—	—19,09	—

When the crystallization points of two substances differ strongly from each other (in the case studied , the crystallization point of (II) is −75.1° and that of (I), −19.1°), it is probable that a eutectic is formed with a temperature close to the crystallization point of one of the components (usually the one with the lower crystallization point) at a low concentration of the second component. This may lead to incorrect conclusions on the

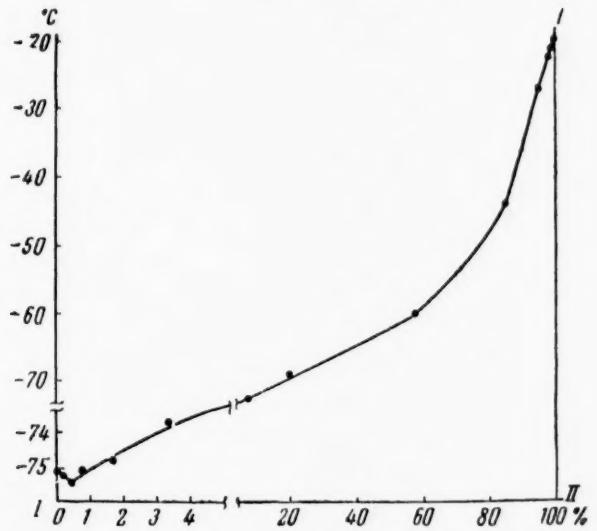

Fig. 3. Melting point diagram of the system cycloheptatriene–bicycloheptadiene. I) 100% cycloheptatriene; II) 100% bicycloheptadiene.

crystallization point and purity of the substance, i.e., an impure substance may be considered pure. However, such cases are rare among systems of organic substances. In the work of Rossini et al., [6], a description was given of the formation of a eutectic mixture of p-xylene (crystallization point +13.26°) and ethylbenzene (crystallization point −94.98°) with a p-xylene concentration of 3.5%. A similar case occurs with the cycloheptatriene–bicycloheptadiene mixture. In actual fact, on continuing the study of the melting point curve of the system (I)–(II), we obtained the data in Table 2. Figure 3 shows that the eutectic point of this system is at a temperature of about −75.5° and corresponds to a mixture containing ~0.5% of bicycloheptadiene.

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CATALYTIC CONVERSION OF 2-ALKYL-5-ACYLFURANS TO ALKYLPHENOLS

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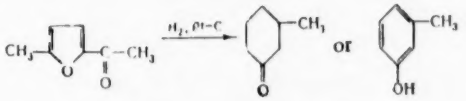
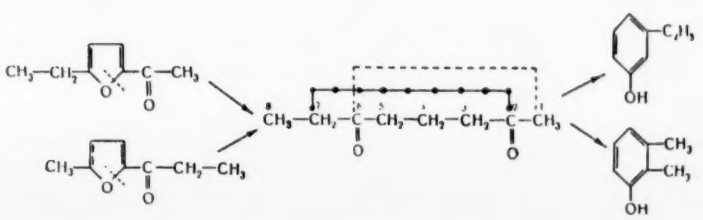
The direction of hydrogenolysis of the furan ring with substituents in the α-position depends on the chemical nature of these substituents. Thus, on the same catalyst, namely, Adam's catalyst, the hydrogenolysis of sylvan and furyl alcohol occurs at the C–O bond remote from the substituent, while hydrogenolysis of pyromucic acid under the same conditions proceeds with rupture of the C–O bond adjacent to the carboxyl group [1]. Hydrogenolysis of 2-alkylfurans over Pt–C in the vapor phase proceeds exclusively at the 1,5 C–O bond with the formation of aliphatic ketones [2]. The results we obtained in the hydrogenation of 2-methyl-5-acetylfuran and methyl pyromucate on a platinum catalyst [3] are of fundamental interest. In both cases the carbonyl-containing group had such an effect that rupture of the furan ring occurred at the C–O bond adjacent to the carbonyl-containing substituent. In this case, methyl pyromucate formed methyl butyrate, while 2-methyl-5-acetylfuran gave 3-methylcyclohexanone or m-cresol, depending on the temperature.



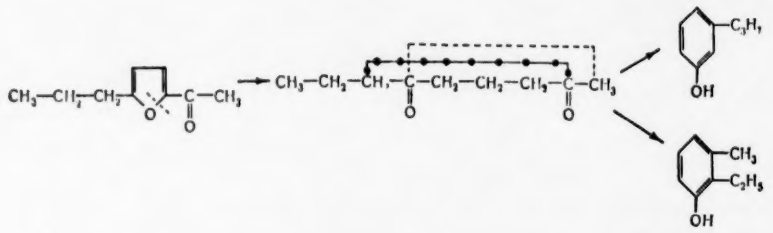
This interesting reaction, which results in the direct conversion of ketones of the furan series into six-membered carbocyclic oxygen-containing compounds, merits further study. In the present work we investigated the catalytic hydrogenation of the following alkylacylfurans over Pt–C in a flow system at normal pressure: 2-acetylfuran, 2-ethyl-5-acetylfuran, 2-methyl-5-propionylfuran, and 2-n-propyl-5-acetylfuran. The hydrogenation was carried out at 300-310°.

In all cases hydrogenolysis of the furan ring occurred at the C–O bond adjacent to the carbonyl group. The 1,5-diketones formed as intermediate products underwent cyclization under the conditions of vapor-phase hydrogenation to form cyclohexenone homologs, which were then dehydrogenated to the corresponding phenol homologs.

In the general case, carbocyclization of unsymmetrical 1,5-diketones may lead to the formation of two isomeric phenols as is shown below on the example of octanedione-2,6.

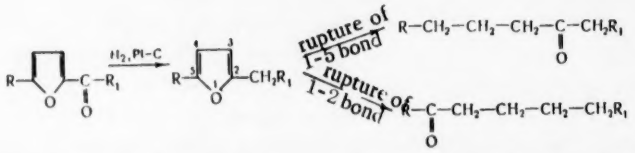


Hydrogenolysis of 2-ethyl-5-acetylfuran and 2-methyl-5-propionylfuran gave as the primary product the same diketone, namely, octanedione-2,6, which, on cyclization with ring closure between carbon atoms 1 and 6, gave 3-ethylphenol and with ring closure between carbon atoms 2 and 7, 2,3-dimethylphenol. Similarly, 2-n-propyl-5-acetylfuran should form 3-n-propylphenol and 2-ethyl-3-methylphenol.

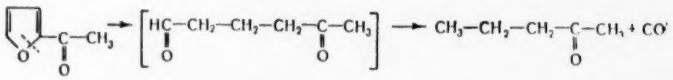


As a result of reduction of the phenols formed from 2-methyl-5-propionylfuran and 2-n-propyl-5-acetylfuran we actually obtained the corresponding hydrocarbons: in the first case, ethylbenzene and o-xylene and in the second, n-propylbenzene and 1-methyl-2-ethylbenzene. Thus, cyclization of unsymmetrical diketones formed as intermediates in the vapor-phase hydrogenation of 2-alkyl-5-acylfurans proceeds in both possible directions with the final formation of mono- and dialkylphenols in each case.

Simultaneously with this main direction of the reaction, there is, to a lesser extent, primary reduction of the carbonyl group with subsequent hydrogenolysis of the furan ring at one of the C–O bonds and the formation of corresponding aliphatic ketones.



2-Acetylfuran occupied a particular position among the compounds investigated. Its hydrogenolysis at the C–O bond adjacent to to the carbonyl group, gave a keto aldehyde, which was not cyclized like a diketone, but decarboxylated completely to pentanone-2.



EXPERIMENTAL

The catalyst, 10% Pt–C, was prepared by impregnating activated birchwood charcoal with chloroplatinic acid solution, followed by reduction in a catalyst tube at 300-350°.

2-Alkyl-5-acylfurans were obtained by acylation of appropriate alkylfurans with acetic or propionic anhydride in the presence of phosphoric acid [4]. They had the following properties:

1. 2-Acetylfuran: b. p. 64-66° (13 mm), m. p. 31-32°.
2. 2-Ethyl-5-acetylfuran: b. p. 93-95° (12 mm), n_D^{20} 1.5067; d_4^{20} 1.0372; semicarbazone: m. p. 167-168°.
3. 2-Methyl-5-propionylfuran: b. p. 100-101° (21 mm), n_D^{20} 1.5063; d_4^{20} 1.0432; semicarbazone: m.p. 155-6°.
4. 2-n-Propyl-5-acetylfuran: b. p. 110-112° (20 mm), n_D^{20} 1.5011; d_4^{20} 1.0102; semicarbazone: m.p. 71°.

The 2-alkyl-5-acylfurans were hydrogenated in a flow system at atmospheric pressure and 300-310° with a space velocity of 0.1 hr^{-1}. The catalyzates were distilled on an efficient column at first at atmospheric and then under reduced pressure.

From the catalyzates of 2-ethyl-5-acetylfuran and 2-methyl-5-propionylfuran we isolated fractions (~60% yield) with b. p. 102-105° (22 mm), 65-67° (3 mm), n_D^{20} 1.5348; d_4^{20} 1.0163, which contained a mixture of 3-ethylphenol and 2,3-dimethylphenol. In addition, the catalyzates contained octanone-2 and octanone-3 (fraction with

b. p. 70-71° (22 mm), n_D^{20} 1.4157; d_4^{20} 0.8231, ~30% yield) and very small amounts of ethylbenzene and o-xylene, which were determined spectroscopically.

The bulk (~60%) of the catalyzate of 2-n-propyl-5-acetylfuran consisted of a phenol fraction with b. p. 122-123° (17 mm), d_4^{20} 0.9931; n_D^{20} 1.5272. It contained 3-n-propylphenol and 3-methyl-2-ethylphenol. We also isolated nonanone-2 and nonanone-3 in a fraction with b. p. 84-86° (19 mm), n_D^{20} 1.4241; d_4^{20} 0.8281; semicarbazone: m. p. 118-119°. n-Propylbenzene and 1-methyl-2-ethylbenzene were detected spectroscopically in a fraction with b. p. 71-78° (20 mm).

The structure of the phenols was determined from the Raman spectra of the aromatic hydrocarbons corresponding to them, which were obtained by reduction of the phenols in a flow system over Pt—C at 330-350°

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*Original Russian pagination. See C. B. translation.

LAW OF CONSTANCY OF THE PRODUCT OF THE ACTIVITIES OF SIMPLE (HYDRATED) METAL IONS AND HYDROXO IONS IN THE HETEROGENEOUS SYSTEM $M^{n+} - M(OH)_{n+m}^{m-} - M(OH)_n - H_2O$

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As all elements are amphoteric, aqueous solutions of ordinary salts contain hydroxo ions together with simple (hydrated) metal ions. Alkaline solutions contain simple metal ions in addition to ions of hydroxo acids. Treatment of salt or metal hydroxide solutions with sodium hydroxide solution gives hydroxo salts. The solubility of the hydroxo salts and the stability of their solutions differ for different metals.

Hydroxo salts are formed by the reaction of salt solutions with sodium hydroxide solution through the successive stages of the formation of hydroxides, hydroxo salts, and their polymeric forms, followed by partial decomposition of the solution to give metal hydroxides [1]. When equilibrium has been established the hydroxo salts remain in solution at concentrations which are determined by the ratio of the alkali and metal concentrations and this remains constant for each metal under given conditions [2]. Polymeric particles disappear by the time the solution decomposes and equilibrium is established in it [3].

The decomposition of hydroxo salt solutions to liberate a hydroxide is spontaneous and therefore the hydroxide precipitated from an alkaline solution is more stable and less soluble both in acids and alkalis. The rate and degree of decomposition are determined mainly by the chemical properties of the metal and the conditions and in the first instance, by the temperature and alkali and salt concentrations. Thus, for example, aluminum, zinc, lead, gallium, and some other metal hydroxides are readily soluble in alkalis. However, if the ratio of alkali to metal concentration is less than a definite value, characteristic of the given metal, these solutions decompose with time to give hydroxides. Other metals, for example, indium, give hydroxo salts (indate), but decomposition begins immediately after preparation.

It is considered that a number of metals do not give hydroxo salts and are insoluble in alkali, for example, iron. Nonetheless, iron hydroxide, as well as other metal hydroxides, also dissolve in alkalis, but the solution decomposes very rapidly and decomposition is practically complete in a very short time. The reason for this may be extensive dehydration of the hydroxide and the hydroxo salt as a result of polarization. As a rule, the more rapidly solutions of hydroxo salts decompose, the smaller the amount of them remaining in solution after decomposition [1, 3].

It is known that in heterogeneous systems, the activity of simple metal ions is related to the solution pH and the product of the activities of the hydroxides by the relation [5]

$$pH = \frac{1}{n} \lg \frac{P_a}{K_w^n a_M}, \quad (1)$$

and the activity of the hydroxo ions by the equation [4]

$$pH = \frac{1}{m} \lg \frac{a_{hy}}{Pa'}, \qquad (2)$$

where a_{hy} is the activity of the hydroxo ions and Pa' and m are the activity product and basicity, respectively, of the hydroxo acid.

Since in the heterogeneous equilibrium the pH refers to the two dissociation processes, namely, of the hydroxide and the hydroxo acid, as these occur in the one solution, the right-hand parts of equations (1) and (2) may be equated and after simple rearrangement, we have:

$$P a^{m/n} \; Pa'/K_w^n = a_M^{m/n} \, a_{hy} = K. \qquad (3)$$

As all the constants are in the right-hand part of equation (3), the left-hand part is also constant. Hence it follows that after the hydroxo salt solution has decomposed, i.e., in the heterogeneous equilibrium established, the product of the activities of the simple (hydrated) metal ions and the hydroxo ions is constant. It should be stressed that such a change in the activity of the ions where the activity of the simple ions falls with an increase in the activity of the hydroxo ions is observed only in solutions saturated with hydroxide with the hydroxide present in a solid phase.

We put forward the hypothesis that in aqueous solutions, the product of the activities of the simple metal ions and the hydroxo ions in an equilibrium heterogeneous system is constant for all metals (which give hydroxo

TABLE 1

Results of Determining the Ionic Product Experimentally

$-\lg a_M$	$-\lg C_{hy}$	$-\lg K$	Linear equations
System: NaOH — $Zn(OH)_2$ — H_2O (1 day)			
12,20	2,12	14,32	$14,1-29,13\,C_{hy}$ $n = m = 2$
12,47	2,09	14,56	
14,22	1,37	15,59	
14,94	1,10	16,04	
System: NaOH — $Zn(OH)_2$ — H_2O (40 days)			
11,96	2,34	14,30	$-14,08-30,2\,C_{hy}$ $n = m = 2$
12,01	2,26	14,27	
13,61	1,51	15,12	
14,39	1,22	15,61	
System: NaOH — $In(OH)_3$ — H_2O			
30,68	4,61	14,84	$-14,06-2\cdot10^3\,C_{hy}$ $n = 3;\ m = 1$
32,74	3,98	14,89	
33,11	4,04	15,08	
System: NaOH — $Ga(OH)_3$ — H_2O			
13,50	2,29	15,81	$-14,02-3,42\,C_{hy}$ $n = m = 3$
12,75	2,54	15,29	
11,96	2,60	14,56	
10,38	3,72	14,10	
System: NaOH — $Pb(OH)_2$ — H_2O			
10,37	3,57	13,94	$-14,10\pm2,71\,C_{hy}$ $n = m = 2$
11,17	2,86	14,03	
11,31	2,59	13,90	
11,61	2,52	14,10	
11,86	2,40	14,26	

salts) and equals the ionic product of water. Naturally, this conclusion applies only to metals which give hydroxo salts.

The hypothesis that the products of the activities of simple and hydroxo ions equals the ionic product of water may be checked experimentally. Using equation (3), one can either calculate this product from the

products of the activities of hydroxides and hydroxo acids or determine it experimentally. The first method of checking the given hypothesis cannot be applied at the present time due to the lack of reliable values for the products of the activities of hydroxo acids. We therefore used the second method, namely, direct determination of the product interesting us.

The experimental procedure was as follows. Freshly prepared metal hydroxide was dissolved in sodium hydroxide solutions of various concentrations. The amount of hydroxide used was such that part of it remained in the solid phase. The solutions were shaken and kept in a thermostat at 25° for 41 days. The activity of the metal ions was then measured potentiometrically with an amalgam dropping electrode. The hydroxo ion concentration was related to the total metal concentration in solution, which was determined analytically. The amalgam electrodes were calibrated against standard solutions of metal perchlorates, in which the ionic activity was calculated from the Debye–Hückel equation. Table 1 gives the results of the measurements.

The activity products obtained were extrapolated to zero hydroxo ion concentration. The logarithms of the ion activity products thus found are given in the form of linear equations. As can be seen, these values of the products of the activities of simple and hydroxo ions equal the ionic product of water and differ from it by not more than 0.1.

We also used a method of determining the product of the activities of simple and hydroxo ions, based on measuring the emf of the cell

$$M(Hg) \mid p\text{-}p\ MA_n + M(OH)_n \mid \underset{\text{sat.}}{KCl} \mid p\text{-}p\ Na_mM(OH)_{n+m} + M(OH)_n \mid M(Hg). \qquad (I)$$

Without considering the diffusion potential, this emf may be expressed by the formula

$$E = \frac{RT}{nF} \ln \frac{a_M}{a'_M}, \qquad (4)$$

where a_M and a'_M are the activities of the metal ions in solutions of the simple salt and hydroxo salt. Substituting the value of a'_M from equation (3) in equation (4) and solving it for lg K, we obtain

$$\lg K = -\frac{mF}{2{,}303\,RT} E + \lg a_M^{m/n} a_{hy}. \qquad (5)$$

There is no need to determine the emf of this cell directly. The electrode potentials of the right and left half-cells may be determined relative to a standard calomel electrode, taking into account the diffusion potential. The value of the emf of cell (I) could be obtained from these data.

TABLE 2

Results of Determining K from the Measured emf of Cell (I)

$-\lg a_{Zn^{2+}}$	$-\lg a_{hy}$	emf	$-\lg K$	$-\lg a_{Pb^{2+}}$	$-\lg a_{hy}$	emf	$-\lg K$
2,0023	2,3042	0,2815	13,83	1,9031	2,6625	0,2802	14,05
2,2043	2,3042	0,2793	13,86	2,3074	2,6625	0,2686	14,06
3,1093	2,3042	0,2532	13,98	2,7618	2,6625	0,2546	14,04
2,0023	3,3468	0,2582	14,09	1,9031	2,8706	0,2735	14,03
2,1043	3,3468	0,2534	14,03	2,3074	2,8706	0,2619	14,04
3,1093	3,3468	0,2239	14,02	2,7618	2,8706	0,2479	14,02
2,0023	3,4216	0,2559	14,08	1,9031	3,9847	0,2395	13,99
2,1043	3,4216	0,2511	14,02	2,3074	3,9847	0,2279	14,00
3,1093	3,4216	0,2226	14,06	2,7618	3,9847	0,2134	13,98
		Average . .	14,00			Average . . .	14,02

If solutions of low concentrations were used, the activity coefficients could be calculated and hence the activities of the ions, then K could be determined from equation (5) (see Table 2).

Thus, we may consider as proved the hypothesis that

$$a_{\text{M}}^{m/n} \, a_{\text{hy}} = K_w. \tag{6}$$

The product of the activities of simple (hydrated) metal ions and hydroxo ions in the heterogeneous equilibrium system $M^{n+} - M(OH)_{n+m}^{m-} - M(OH)_2 - H_2O$ is constant and equal to the ionic product of water at a given temperature.

From this rule we can calculate the activity products of hydroxo acids, the instability constants of hydroxo ions, and the number of hydroxyl ions coordinated around a central metal ion and hence the basicity of hydroxo acids, the isobaric-isothermal potentials of hydroxo ion formation, the pH of the isoelectric points of hydroxides, and a number of other values.

To determine the activity product of hydroxo acids it is necessary to solve the equation $Pa^{m/n} pa'/K'_w = K_w$ with respect to Pa'

$$Pa' = K_w^{m+1}/Pa^{m/n} \tag{7}$$

The instability constant is expressed by the equation

$$K_i = PaK_w^m/Pa'. \tag{8}$$

By replacing a' in this equation by the expression for it from equation (7), we obtain

$$K_i = P a^{\frac{n+m}{n}} / K_w. \tag{9}$$

Thus, the instability constants of hydroxo ions may be calculated from equation (9). Similarly, the pH values of the isoelectric points of hydroxides may be calculated. The isobaric potentials of hydroxo ion formation may be calculated from equation (6).

$$\Delta Z^0_{\text{hy}} = \Delta Z^0_{\text{M(OH)}_n} + m\Delta Z^0_{\text{OH}'} - 2{,}3\,RT \lg P a' + 2{,}3\,mRT \lg K_w. \tag{10}$$

By substituting the value of Pa' from equation (7) in this equation, we obtain

$$\Delta Z^0_{\text{hy}} = \Delta Z^0_{\text{M(OH)}n} + m\Delta Z^0_{\text{OH}'} + 2{,}3\,\frac{m}{n}\,RT \lg P a - 2{,}3\,RT \lg K_w. \tag{11}$$

TABLE 3

Calculated Values of Pa', K_i, and ΔZ^0_{hy} of Some Hydroxo Acids and Ions

Hydrogen ion	lg Pa	Pa'	K_i	ΔZ^0_{hy}, kcal/mole
$Zn(OH)_4^{2-}$	—17,4 [7]	$2{,}51 \cdot 10^{-25}$	$6{,}31 \cdot 10^{-21}$	—216,40
$Pb(OH)_4^{2-}$	—15,35 [8]	$2{,}24 \cdot 10^{-27}$	$5{,}01 \cdot 10^{-17}$	—178,91
$Al(OH)_4^-$	—31,70 [9]	$3{,}72 \cdot 10^{-18}$	$5{,}01 \cdot 10^{-29}$	—303,89
$In(OH)_4^-$	—36,92 [10]	$2{,}04 \cdot 10^{-16}$	$5{,}89 \cdot 10^{-36}$	—222,10
$Ga(OH)_6^{3-}$	—36,29	$1{,}95 \cdot 10^{-20}$	$2{,}63 \cdot 10^{-59}$	—342,02

As can be seen, we need to know only the activity products of the hydroxides, which are known for most metals, to calculate the values given above. The calculated values for some hydroxo acids and ions are given in Table 3 as examples.

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HYDROLYSIS KINETICS OF SOME COMPLEX COMPOUNDS OF Pt (IV)

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Kinetic investigations of substitution reactions in complex compounds of Pt (IV) were begun by Zvyagintsev and Karandasheva in 1956 [1]. Of the earlier work, we should note a qualitative study of the kinetics of hydrolysis of chloro- and bromoplatinate [2-4]. Basolo and Pearson et al., recently published brief communications on kinetic investigations of the hydrolysis of trans-$[Pt\ en_2{}^{*}Cl_2]^{+2}$ [5, 6]. In this work it was reported that the hydrolysis of the dichlorodiethylenediamine ion is zero order reaction with respect to the alkali concentration. The complex concentration was not varied. The hydrolysis rate was determined from the concentration of chlorine ions in the solution. On this basis, an S_N1CB mechanism, which may be represented in the following way:

$$[Pt\ en_2\ Cl_2]^{+2} + OH' \rightleftarrows [Pt\ en\ (en - H)\ Cl_2]^{+1} + H_2O \quad \text{(fast)}$$
$$[Pt\ en\ (en - H)\ Cl_2]^{+1} \rightleftarrows [Pt\ en\ (en - H)\ Cl]^{+2} + Cl' \quad \text{(slow)}$$
$$[Pt\ en\ (en - H)\ Cl]^{+2} + H_2O \rightleftarrows [Pt\ en_2\ ClOH]^{+2} \quad \text{(fast)}$$

was proposed for the hydrolysis of trans-$[Pt\ en_2Cl_2]^{+2}$. By studying the isotopic exchange of chlorine in the same compound, trans-$[Pt\ en_2Cl_2]^{+2}$, Basolo and Pearson established the catalytic effect of traces of divalent platinum on the exchange rate and the lack of effect of added Pt (II) on the hydrolysis rate.

The purpose of the present work was to study the kinetics of hydrolysis of complexes forming the Werner–Miolath transition series: $Na_2[PtCl_6]$, $k[PtNH_3Cl_5]$, $[Pt(NH_3)_2Cl_4]$, $[Pt(NH_3)_3Cl_3]Cl$ (Cleve's salt), trans-$[Pt(NH_3)_4Cl_2](NO_3)_2$, $[Pt(NH_3)_5Cl]Cl_3$, and the pyridine complex $K[PtPy^{**}Cl_5]$. The isomeric diamines in this series have not yet been studied due to their low solubility. Experiments on hydrolysis kinetics were carried out in the dark in vessels covered with red lacquer. The hydrolysis rate was followed through the alkali reacting by visual titration. Phenolphthalein was used as indicator in all cases apart from that of the chloropentamine, where methyl orange was used.

Together with a high resistance to substitution reactions, for complex compounds of Pt (IV) one might expect a more complex hydrolysis picture than that which the authors observed for compounds of Pt (II) [7]. Complication of the hydrolysis of Pt (IV) complexes should be caused by the increase in the number of coordinated groups capable of replacement, by the presence of sharply expressed acidic properties, and by the possibility of redox processes. The latter can play a major role in some isomerization and substitution reactions [8, 9]. Experimental investigations actually demonstrated the great diversity of the hydrolysis kinetics of the individual members of the series studied.

The relation between the hydrolysis rate and the alkali concentration was of the first order for $k[PtNH_3Cl_5]$, $[Pt(NH_3)_4Cl_2](NO_3)_2$ and approximately for $[Pt(NH_3)_5Cl]Cl_3$. For $k[PtPyCl_5]$ and $[Pt(NH_3)_3Cl_3]Cl$ the hydrolysis rate was independent of alkali concentration. Even these results indicate that there is not the same diversity in the hydrolysis mechanism for Pt (IV) compounds as was observed for Pt (II) compounds [7]. A relation between the hydrolysis rate and the complex concentration to the power one was observed for $k[PtPyCl_5]$ and $[Pt(NH_3)_5Cl]Cl_3$, and to the power 1.75 for $k[ptNH_3Cl_5]$, $[Pt(NH_3)_3Cl_3]Cl$ and $[Pt(NH_3)_4Cl_2](NO_3)_2$. Together with the unusually high order of hydrolysis rate of the mono-, tri-, and tetramines with respect to the

*en denotes ethylenediamine.

**Py denotes pyridine.

complex concentration, during the hydrolysis these compounds were partly reduced to Pt (II) compounds. At the end of reaction at 25°, from 1 to 5% of the original complex was reduced. An increase in temperature increased the reduction. It should be noted that in a qualitative comparison of the hydrolysis rates of the complexes studied, $k[PtNH_3Cl_5]$, $[Pt(NH_3)_3Cl_3]Cl$, and $[Pt(NH_3)_4Cl_2](NO_3)_2$ showed the highest rates.

At the concentrations studied, the chloroplatinate, pyridine monoamine, and pentamine were not reduced by alkali even on heating. The high order of the hydrolysis rate of $k[PtNH_3Cl_5]$, $[Pt(NH_3)_3Cl_3]Cl$, and $[Pt(NH_3)_4Cl_2](NO_3)_2$ may be explained by the presence of redox processes in the system and, in particular, the formation of molecular compounds of the type $[Pt(NH_3)_3Cl_3]Cl \cdot [Pt(NH_3)_3Cl]Cl$. It may be thought that some sort of "active" complexes may participate in the given reactions somehow or other. Since this aspect of the problem has not been elucidated completely as yet, in interpreting the mechanisms of the reactions of the compounds examined it will be considered provisionally that the original complex participates in the reaction. Considering this, for $k[PtNH_3Cl_5]$ we may put forward the following mechanism for the hydrolysis:

$$[PtNH_3Cl_5]^{-1} + OH' \rightleftarrows [PtNH_2Cl_5]^{-2} + H_2O \quad \text{(fast)}$$
$$[PtNH_2Cl_5]^{-2} + H_2O \rightleftarrows [PtNH_2Cl_4H_2O]^{-1} + Cl' \quad \text{(slow)}$$
$$[PtNH_2Cl_4H_2O]^{-1} \rightarrow [PtNH_3Cl_4OH]^{-1} \quad \text{(fast)}$$

A similar hydrolysis mechanism may be proposed for $[Pt \cdot (NH_3)_3Cl_3]^{+1}$. The difference in the relation of the hydrolysis rates to alkali concentration with $k[PtNH_3Cl_5]$ and $[Pt(NH_3)_3Cl_3]Cl$ may be explained by the fact that the acidic properties of the triamine must be expressed more strongly than the acidic properties of the monoamine and, consequently, the acid–base equilibrium (1st stage) must be displaced more strongly to the right.

The hydrolysis mechanism of $[Pt(NH_3)_4Cl_2]^{+2}$ may include the direct replacement of chlorine in $[Pt(NH_3)_3NH_2Cl_2]^{+1}$ by hydroxyl. The coulombic attraction of oppositely charged ions should promote such a replacement. The mechanism of the hydrolysis of $[Pt(NH_3)_5Cl]Cl_3$ (second order reaction) does not require the assumption of the condition which was applied to previous complexes. The most probable mechanism is as follows:

$$[Pt(NH_3)_5Cl]^{+3} + OH' \rightleftarrows [Pt(NH_3)_4NH_2Cl]^{+2} + H_2O \quad \text{(fast)}$$
$$[Pt(NH_3)_4NH_2Cl]^{+2} + OH' \rightleftarrows [Pt(NH_3)_4NH_2OH]^{+2} + Cl' \quad \text{(slow)}$$
$$[Pt(NH_3)_4NH_2OH]^{+2} + H_2O \rightleftarrows [Pt(NH_3)_5OH]^{+3} + OH' \quad \text{(fast)}$$

According to this mechanism, the occurrence of the reaction requires excess alkali above the one equivalent consumed in the formation of the amide. This idea is in agreement with experimental data.

The hydrolysis of $k[PtPyCl_5]$, probably proceeds in the following way:

$$[PtPyCl_5]^{-1} + H_2O \rightleftarrows [PtPyCl_4H_2O]^{0} + Cl' \quad \text{(slow)}$$
$$[PtPyCl_4H_2O]^{0} + OH' \rightleftarrows [PtPyCl_4OH]^{-1} + H_2O \quad \text{(fast)}$$

According to [2] the rate of hydrolysis of chloroplatinate is so low that after a measured time the amount of alkali that had reacted was within the limits of experimental error. However, a qualitative comparison of the hydrolysis rates of $Na_2[PtCl_6]$, $k[PtPyCl_5]$ and $k[PtNH_3Cl_5]$ (with identical concentrations) showed that in this series the reaction rate increased from chloroplatinate to pyridine monoamine and further to the ammonia monoamine.

At the beginning of the article we considered the investigation of Basolo and Pearson of the hydrolysis kinetics of trans-$[Pten_2Cl_2]^{+2}$. On comparing the results for the hydrolysis kinetics of $[Pt(NH_3)_4Cl_2]^{+2}$ with the results of Basolo and Pearson for the hydrolysis of trans-$[Pten_2Cl_2]^{+2}$ the authors were unable to understand the difference in the relations of the hydrolysis rates of these compounds to alkali concentration. It therefore seemed necessary to compare the hydrolysis rates of trans-$[Pt(NH_3)_4Cl_2]^{+2}$ and trans-$[Pten_2Cl_2]^{+2}$. In these investigations it was found that during the hydrolysis of trans-$[Pten_2Cl_2]^{+2}$, together with an increase in the chlorine ion concentration, there appeared in the solution considerable amounts of $[Pten_2]^{+2}$, which is the reduction product of the starting complex. Further investigations of the kinetics of the reaction of trans-$[Pten_2Cl_2]^{+2}$ with alkali were carried out with a parallel study of the alkali consumption, increase in the chlorine ion concentration, and accumulation of divalent platinum in solution with time. Our investigations showed that all these three processes proceeded at approximately identical rates.

Thus, the S_N1CB mechanism for the hydrolysis of trans-$[Pten_2Cl_2]^{+2}$ does not reflect the processes occurring in the solution. The mechanism of the reaction of trans-$[Pten_2Cl_2]^{+2}$ with alkali is much more complex. These investigations are being completed at the present time and their results will be published soon.

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REDUCTION OF MANGANESE FERRITE WITH HYDROGEN AND GRAPHITE

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Manganese ferrite has a crystal lattice of the spinel type in which the metal ions can exist in different valence states [1] and the oxygen content may deviate from the stoichiometric value [2]. Manganese ferrite is widely used as it is the basis for the preparation of materials with valuable magnetic properties. Its formation conditions have been studied by many investigators [3, 4]. The ferrite of stoichiometric composition was obtained by firing a mixture of oxides in a carbon dioxide atmosphere [4].

The starting material for the present investigation was manganese ferrite obtained by sintering an equimolar mixture of Fe_2O_3 and MnO at 1200° for 30 hr. The firing and cooling were carried out in a stream of CO_2. X-ray structural analysis of the product obtained showed that it consisted of one phase and had a lattice parameter of 8.50 A, which agrees with the literature data [5].

Sintering in air yielded a single-phase ferrite with a parameter of 8.452 A, i.e., considerably less, which indicates a higher oxygen content of the lattice than the stoichiometric value.

Reduction of manganese ferrite with hydrogen. Manganese ferrite was reduced with hydrogen in a closed apparatus with gas circulation. The water vapor formed was frozen out in a trap cooled with liquid gas. The reaction rate was determined from the decrease in hydrogen pressure. The reduction was carried out at 400 and 500° and an initial hydrogen pressure of 400 mm.

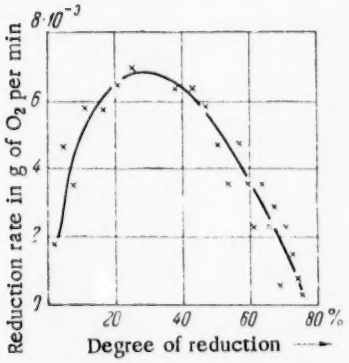

Fig. 1. Reduction of manganese ferrite with hydrogen at 500°.

The rate of manganese ferrite reduction first increased as the reduction proceeded, reached a maximum value at approximately 30-40% removal of the oxygen (Fig. 1), and then it began to fall and the process practically stopped when 75% of the oxygen had been removed from the ferrite. X-ray structural analysis showed that this sample contained metallic iron and manganous oxide.

Reduction of manganese ferrite with graphite. The reducing agent was graphite powder obtained by grinding Acheson electrodes and fired in vacuum at 1000°. A mixture of 0.3*of ferrite and 0.2*of graphite was mixed carefully and placed in a quartz bucket, suspended from McBain balances. A vacuum of the order of 10^{-2} mm was maintained in the reaction space during the experiment. The reaction rate was determined from the weight loss and the amount of CO_2 liberated, which was collected in a trap cooled with liquid nitrogen.

As the reduction proceeded, the rate decreased (Fig. 2) and there was a clearly expressed minimum on the kinetic curve at about 25%. With further reduction, the rate increased somewhat and then fell to zero at the end of the process. Manganese ferrite was reduced completely by graphite at 1000°. X-ray structural

*Unit omitted in Russian. – Publisher.

analysis of ferrite samples reduced to different extents showed that the spinel phase was detected only up to 20% reduction. The x-ray diffraction pattern of a sample reduced 20% showed only weak lines belonging to the spinel phase and clearly expressed lines of a lattice of the NaCl type. Possible phases with a lattice of this type are ferrous or manganous oxides or their solid solutions. No metallic phase was detected at this stage. Samples reduced more than 20% contained two phases, a lower oxide phase and a metallic phase. The parameters of the crystal lattices of these phases did not change with an increase in the percent reduction, indicating the presence of solid solutions of constant concentration.

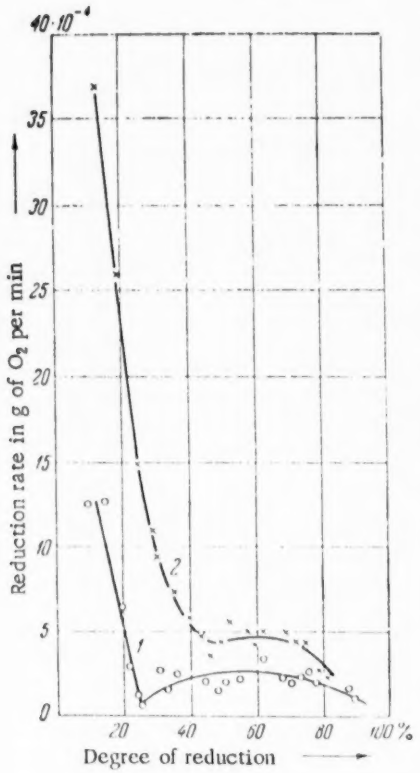

Fig. 2. Reduction of manganese ferrite with graphite: 1) without additive; 2) with K_2CO_3 added.

As the manganese to iron ratio in the ferrite did not exceed 35 at. %, according to the phase diagram of the Mn–Fe system [6], the γ-solid solution should be most stable at 1000°. The x-ray diffraction patterns showed a predominant amount of the α-solid solution, which was formed as a result of decomposition of the γ-solution on cooling.

The gaseous reduction products liberated during the reduction of manganese ferrite with graphite initially contained about 70% of CO_2. As the reduction proceeded, the carbon dioxide content fell and after 25% reduction the gaseous reaction products contained only carbon monoxide.

Effect of additives on the reduction of manganese ferrite with graphite. Potassium and sodium carbonates were tested as additives. The additive (1% of the weight of ferrite) was carefully ground with the ferrite and graphite. The reduction was carried out by the same procedure as without the additive. Additions of potassium and sodium carbonates had an accelerating action on the reduction of manganese ferrite (Fig. 2). X-ray diffraction studies were carried out on the solid products from the reduction of manganese ferrite with K_2CO_3 added. The phase with a spinel type lattice, analogous to the starting ferrite, was present in a sample 18.93% reduced, but was not detected at 28.9% reduction.

In all the samples we detected a phase with a NaCl type lattice, corresponding to the lower oxide phase MnO. Its parameter increased with an increase in the percent reduction, approaching the parameter of the MnO lattice, but not reaching it (Fig. 3). At 89.9% reduction the lattice of this phase was strongly distorted and the lattice parameter was not determined. A metallic phase could be detected first at 30% reduction. This phase had a body-centered cubic lattice of the α-Fe type, whose parameter first increased slightly and then remained constant on reaching a value of 2.865 A, indicating that its concentration was constant. A sample 90% reduced showed a γ-solid solution with a lattice parameter of 3.618 A.

On the basis of the experimental material presented above, the mechanism of manganese ferrite reduction may be represented as follows. The removal of oxygen from the surface of the crystal lattice produces an excess of metal ions, which, on the one hand, may diffuse into the depth of the ferrite lattice and, on the other hand, may form a metallic phase. The occurrence of one or other process depends on the ratio of the rates of removal of oxygen and reaction diffusion.

During reduction by hydrogen, the rate of oxygen removal exceeds the diffusion rate as the process occurs at comparatively low temperatures (400-500°). The ions formed on the surface are unable to diffuse into the ferrite lattice and part of them form the nuclei of a metallic phase. Iron ions pass predominantly into the metallic phase as they are less firmly bound to oxygen. Manganese ions, diffusing into the lattice, convert it into a lattice of the NaCl type, characteristic of a $MnFe_{1-x}O$ solid solution. The latter is gradually enriched in

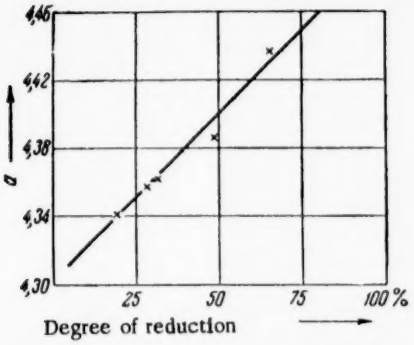

Fig. 3. Relation between the lattice parameter of the lower oxide phase and the degree of reduction.

manganese and approaches an MnO lattice. Further reduction of MnO does not occur at this temperature and the process practically ceases when 75% of the oxygen has been removed from the oxide.

In the reduction by graphite in vacuum at 1000°, the rate of oxygen removal is commensurate with the diffusion rate. Metallic ions can diffuse into the depth of the spinel lattice and convert it into a lattice of the NaCl type. A metallic phase is formed only after this conversion is complete (i.e., after 25% reduction) and forms a solid solution of manganese in iron of constant concentration.

The addition of potassium and sodium carbonates accelerates the reduction process. The single-zone nature of the process, characteristic of reduction by graphite [7, 8] disappears and the metallic phase appears earlier than in reduction without additives, i.e., before 25% reduction. The metallic phase is formed predominantly from iron ions and therefore the lower oxide phase developing is enriched in manganese as indicated by the increase in the lattice parameter.

With further reduction the manganese also passes into the metallic phase, forming a γ-solid solution, which decomposes on cooling, and lines of the α-phase are obtained on the x-ray diffraction patterns. With an increase in the manganese concentration, the γ-phase becomes stable and does not decompose on cooling, and therefore at 90% reduction, lines of the γ-phase are detected on the x-ray diffraction patterns.

Thus, in the case of manganese ferrite reduction the addition of alkali metal salts accelerates the stage of the chemical reaction of the reducing agent with the compound reduced, which is caused by a change in the electronic state of the lattice due to the penetration of monovalent ions into it [9].

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SOME CONVERSIONS OF 1,5,9-CYCLODODECATRIENE

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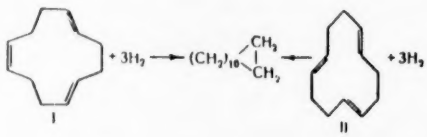
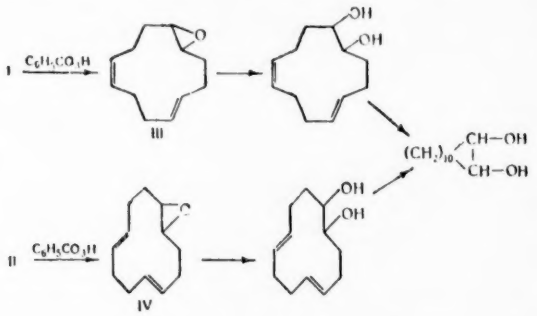
By cyclotrimerization of butadiene, Wilke [1, 2] obtained two isomers of 1,5,9-cyclododecatriene, to which he assigned the structures of cis-trans-trans-1,5,9-cyclododecatriene (I) and trans-trans-trans-1,5,9-cyclododecatriene (II) on the basis of the infrared spectra. In the present work we studied some conversions of these cyclododecatriene isomers. Both isomers were hydrogenated smoothly at atmospheric pressure and room temperature over Pt and Pd catalysts and also over Raney Ni to give a quantitative yield of cyclododecane.



The hydrogenation of the two isomers proceeded at practically the same rate. The rate of hydrogenation of the double bonds of I and II over $Pd/CaCO_3$ and $Pd/BaSO_4$ in alcohol solution was almost the same. The rate of hydrogenation of the double bonds on Raney Ni in alcohol solution gradually decreased.

Potassium permanganate oxidation of the mixture of hydrogenation products of I, obtained after the absorption of 2 moles of hydrogen per mole of I, gave a 30% yield of 1,10-decanedicarboxylic acid. The action of perbenzoic acid on I and II gave the corresponding monoxides. I formed the liquid oxide III and II gave the crystalline oxide IV. Opening of the oxide ring with formic acid and subsequent hydrolysis with alkali solution gave cis-trans-5,9-cyclododecadiene-cis-1,2-diol from III and trans-trans-5,9-cyclododecadiene-cis-1,2-diol from IV. Hydrogenation of both diols gave the known cyclododecane-cis-1,2-diol [3].



Thus, epoxidation of cis-trans-trans-cyclododecatriene proceeded selectively, leading to the formation of the trans oxide (III). Reduction of the double bonds in III yielded trans-epoxycyclododecane, which gave cyclododecane-cis-1,2-diol when the oxide ring was opened.

The bromination of both isomers was studied. The best results were obtained by bromination in glacial acetic acid. The action of three moles of bromine on one mole of I apparently formed a mixture of different geometric isomers of hexabromocyclododecane, from which we were able to isolate a crystalline hexabromide with m. p. 194-195°. After the action of bromine on II, from the mixture we isolated a hexabromocyclododecane with m. p. 177-178°. With silver nitrate, I and II gave crystalline complexes with the composition $C_{12}H_{18} \cdot AgNO_3$.

EXPERIMENTAL

The addition of cis-trans-trans-cyclododecatriene to an alcohol solution of silver nitrate gave a crystalline adduct with m. p. 166-167 (from alcohol).

Found %: C 43.62; 43.57; H 5.58; 5.45. $C_{12}H_{18}AgNO_3$. Calculated %: C 43.39; H 5.42.

The addition of trans-trans-trans-cyclododecatriene to an alcohol solution of silver nitrate gave an adduct with m. p. 198-199° (decomp.) (from alcohol).

Found %: C 42.92; 42.93; H 5.37; 5.47. $C_{12}H_{18}AgNO_3$. Calculated %: C 43.39; H 5.42.

Hydrogenation of 1,5,9-cyclododecatriene. a) 20 g of cis-trans-trans-cyclododecatriene in 50 ml of ethyl alcohol was hydrogenated over 0.4 g of 5% $Pd/BaSO_4$ at atmospheric pressure and room temperature; we obtained 19.2 g of cyclododecane with m. p. 60-61° (from alcohol). b) 20 g of cis-trans-trans-cyclododecatriene in 50 ml of ethyl alcohol was hydrogenated over 2 g of Raney nickel at atmospheric pressure and room temperature; we obtained 18.7 g of cyclododecane with m. p. 60-61° (from alcohol). Literature data [4]: m. p. 60-61°. c) 320 g of cis-trans-trans-cyclododecatriene in 150 ml of ethyl alcohol was hydrogenated in a 2-liter autoclave over 20 g of Raney nickel at a hydrogen pressure of 100 atm and room temperature; we obtained 320 g of cyclododecane.

The hydrogenation of trans-trans-trans-cyclododecatriene proceeded similarly.

1,10-Decanedicarboxylic acid. A solution of 50 g of I in 100 ml of ethyl alcohol was hydrogenated over 20 g of 1% $Pd/CaCO_3$ until 14.8 liters of hydrogen had been absorbed. We obtained 50 g of a mixture of hydrogenation products. A solution of 38.2 g of $KMnO_4$ in 725 ml of water was added gradually at 25-30° to 15 g of this mixture in 150 ml of water. After 2 hr the manganese dioxide was removed by filtration and the filtrate evaporated to 200 ml and acidified with hydrochloric acid. The precipitate was collected and recrystallized from water. We obtained 6.1 g of 1,10-decanedicarboxylic acid with m. p. 126-127°. Literature data [5]: m. p. 126.5-127°.

Epoxidation of cis-trans-trans-cyclododecatriene. To a solution of perbenzoic acid (from 100 g of benzoyl peroxide) in chloroform at 0° was gradually added 50 g of I. The solution was kept at 0° for 2 hr and then at 20° for 12 hr. The chloroform solution was washed with dilute sodium hydroxide solution and water and dried over calcium chloride. Vacuum distillation yielded 22.5 g of monoepoxide with b. p. 100-101° at 3 mm, n_D^{20} 1.5038; d_4^{20} 0.9743.

Found %: C 81.07; 81.00; H 10.20; 10.01. $C_{12}H_{18}O$. Calculated %: C 80.89; H 10.11

cis-trans-trans-Cyclododecadiene-cis-1,2-diol. 10 g of epoxide from the previous experiment was dissolved in 30 ml of 96% formic acid. Heat was evolved during the reaction. After the mixture had been heated for 30 min at 45-55°, the formic acid was removed in vacuum and a solution of 15 g of sodium hydroxide in 25 ml of water and 5 ml of alcohol added to the residue. The mixture was stirred and heated at 60-70° for an hour. Water was added to the cool solution and the solid precipitate of diol collected, washed with water, and dried. We obtained 9.8 g of diol with m. p. 159-159.5° (from alcohol + benzene).

Found %: C 73.39; 73.30; H 10.05; 10.12. $C_{12}H_{20}O_2$. Calculated %: C 73.47; H 10.20.

A solution of 1 g of diol in 10 ml of ethyl alcohol was hydrogenated over 0.2 g of $Pd/BaSO_4$. We obtained 1 g of cyclododecane-cis-1,2-diol with m. p. 159-160° (from aqueous alcohol). Literature data [3]: m. p. 159-160°.

Epoxidation of trans-trans-trans-cyclododecatriene. To a solution of perbenzoic acid (from 25 g of benzoyl peroxide) in chloroform at 0° was added 14 g of II. The solution was kept at 0° for 2 hr and at 20° for

12 hr. The chloroform solution was washed with dilute sodium hydroxide solution and water and dried over calcium chloride. Vacuum distillation yielded 4.8 g of epoxide with b. p. 100-101° at 3 mm and m. p. 31-32° (from ligroin).

Found %: C 80.72; 80.53; H 10.20; 9.98. $C_{12}H_{18}O$. Calculated %: C 80.89; H 10.11.

trans-trans-Cyclododecadiene-cis-1,2-diol. A solution of 0.9 g of epoxide from the previous experiment in 10 ml of 96% formic acid was heated at 45-55° for 2 hr. The formic acid was removed in vacuum and the residue treated with 15 ml of 40% sodium hydroxide solution at 50-60°. After dilution of the reaction mixture with water, the solid precipitate of diol was collected, washed with water, and dried. We obtained 0.8 g of diol with m. p. 130-131° (from alcohol + benzene).

Found %: C 73.39; 73.30; H 10.05; 10.12. $C_{12}H_{20}O_2$. Calculated %: C 73.47; H 10.20.

Hydrogenation of 0.5 g of diol in 10 ml of ethyl alcohol over 0.2 g of $Pd/BaSO_4$ yielded 0.5 g of cyclododecane-cis-1,2-diol with m. p. 160°.

trans-Epoxycyclododecane. A solution of 8.6 g of trans-epoxy-cis-trans-cyclododecadiene in 40 ml of methanol was hydrogenated over 3.2 g of 1% $Pd/CaCO_3$ until the calculated amount of hydrogen had been absorbed. Vacuum distillation yielded 5.3 g of trans-epoxycyclododecane with b. p. 100-102° at 3 mm, n_D^{20} 1.4775; d_4^{20} 0.9424.

Found %: C 79.45; 79.56; H 11.97; 12.11. $C_{12}H_{22}O$. Calculated %: C 79.12; H 12.08.

Treatment of the epoxide obtained with formic acid and then sodium hydroxide solution as described above in analogous experiments yielded cyclododecane-cis-1,2-diol with m. p. 160°.

Bromination of cis-trans-trans-cyclododecatriene. To a solution of 16 g of I in 30 ml of acetic acid was gradually added 44 g of bromine with stirring at 10-12°. A finely crystalline precipitate gradually formed and this was collected and washed with acetic acid. We obtained 14 g of a product with m. p. 148-156°. Recrystallization from benzene yielded two bromides: hexabromocyclododecane with m. p. 194-195°

Found %: C 22.66; 22.88; H 2.84; 2.86; Br 74.54; 74.51. $C_{12}H_{18}Br_6$. Calculated %: C 22.42; H 2.80; Br 74.76.

and a tetrabromide with m. p. 162-163°.

Found %: C 29.91; 29.71; H 3.83; 3.57; Br 66.79; 66.43. $C_{12}H_{18}Br_4$. Calculated %: C 29.87; H 3.73; Br 66.39.

The mixture of bromides in the active acid mother liquor was a viscous oil which could not be distilled without decomposition and from which we could not isolate other crystalline compounds.

Bromination of tran-trans-trans-cyclododecatriene. To a solution of 27 g of II in 80 ml of acetic acid was gradually added 80 g of bromine with stirring at 12-15°. At the end of the bromination, the temperature was raised to 35-40°. The solution obtained was poured into water and the solid precipitate collected and washed with water. To remove water, the bromide was triturated with methanol and then ethanol, collected on a filter, and dried in air. We obtained 100 g of dry product, which gave 37 g of hexabromocyclododecane when recrystallized from a mixture of benzene and ethanol. The remaining product was a greasy residue, which could not be crystallized. The hexabromocyclododecane obtained had m. p. 177-178° (from acetic acid).

Found %: C 22.54; 22.67; H 2.84; 2.86; Br 74.71; 74.64. $C_{12}H_{18}Br_6$. Calculated %: C 22.42; H 2.80; Br 74.76.

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STRUCTURE OF SOME REACTION PRODUCTS OF ALKYLALUMINUMS AND TITANIUM (IV) DERIVATIVES

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We recently [1] described the electron paramagnetic resonance spectra of the reaction products of triisobutylaluminum and dicyclopentadienyltitanium dichloride. Further investigation made it possible to extend the observed rules to other compounds and to draw some conclusions on the structure of the reaction products.

We investigated the reaction of the alkylaluminums and arylaluminums $Al(C_6H_5)_3$; $Al(iso\text{-}C_3H_7)_3$; $Al(CH_3)_3$; $Al(iso\text{-}C_4H_9)_3$; $Al(C_2H_5)_2Cl$ with the titanium (IV) derivatives $(C_5H_5)_2TiCl_2$; $(C_5H_5)_2TiBr_2$; $(C_5H_5)_2TiI_2$.

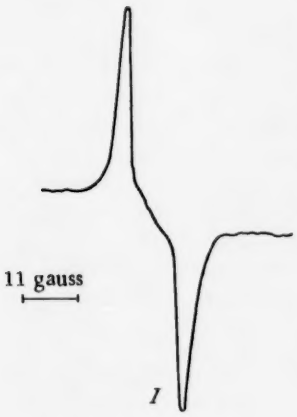


Fig. 1.

With a reagent ratio of 1 : 1 in toluene solution, in all cases we obtained very similar electron paramagnetic resonance signals with a g value equal to 1.975. At low reagent concentrations (less than $1 \cdot 10^{-3}$ M) the signals had a characteristic form (Fig. 1), which could be explained by the presence of an unresolved hyperfine structure. A study of the electron paramagnetic resonance spectra for other Al/Ti ratios showed that the alkylaluminums and arylaluminums could be divided into two groups. With an increase in the Al/Ti ratio, in the case of $Al(CH_3)_3$, $Al(C_6H_5)_3$, and $AlCl(C_2H_5)_2$ signal I (Fig. 1) did not change appreciably, while in the case of $Al(C_2H_5)_3$, $Al(iso\text{-}C_3H_7)_3$, and $Al(iso\text{-}C_4H_9)_3$ new signals were formed with a well resolved hyperfine structure. In the latter systems, with a change in Al : Ti from 1 : 1 to ~20 : 1, there was a change of signal I (Fig. 1) to signal II (Fig. 2a), which is a doublet with a g value equal to 1.985. With an increase in the Al : Ti ratio to ~50 : 1 and above, there was a further change of signal II to signal III with a g value of 1.988, which consisted of eight components (Fig. 3a). The form of signals II and III did not depend on the nature of the alkyl of the alkylaluminums of the second group or the nature of the halogen atom for the titanium halides.

The change I → II → III was observed both with an increase in the AlR_3 concentration with a constant $(C_5H_5)_2TiCl_2$ concentration and with a decrease in the $(C_5H_5)_2TiCl_2$ concentration at a constant alkylaluminum concentration. This effect of the reagent ratios naturally resulted in the hypothesis that the alkylaluminums contained some sort of identical impurities, the amounts of which became comparable with the amounts of titanium derivative with an increase in the Al : Ti ratio and which formed new complexes with the latter.

Such impurities could be hydrides, which are known to be formed readily in the preparation of $Al(C_2H_5)_3$, $Al(iso\text{-}C_3H_7)_3$, and $Al(iso\text{-}C_4H_9)_3$ and are absent in the case of $Al(CH_3)_3$ and $Al(C_6H_5)_3$.

To check this hypothesis we synthesized $AlH(iso\text{-}C_4H_9)_2$ and studied its reaction with $(C_5H_5)_2TiCl_2$. At a Al : Ti ratio of 1, a signal of type I was again observed, but even at ratios of 2 : 1 and 3 : 1 signals II and III were obtained. This left no doubt on the participation of aluminum hydrides in the formation of complexes

corresponding to signals II and III. Doublet II could then be explained by splitting at the hydrogen atom in a complex containing one molecule of $AlH(iso\text{-}C_4H_9)_2$.

Signal III was more complex. As can be seen from Fig. 3a, it consisted of six lines of approximately equal intensity and of two lines with an intensity and of two lines with an intensity a factor of 3-4 less.

As we have already pointed out [1], this hyperfine structure may be explained by distribution of the spin density of the unpaired electron between the Al atom and two H atoms. Now this is naturally explained by the fact that the molecule of the reaction product contains two H atoms from two molecules of aluminum hydride.

Further confirmation of the participation of hydride hydrogen in the complexes formed was provided by experiments with deuterated diisobutylaluminum hydride with the composition $AlD[CH_2CD(CH_3)_2]_2$. The electron paramagnetic resonance spectra of the reaction products of this compound and $(C_5H_5)_2TiCl_2$, corresponding to signals II and III, are given in Figs. 2b and 3b. It can be seen that replacement of hydrogen by deuterium led to almost complete disappearance of the hyperfine structure in both cases. The nuclear moment of the D atom is a factor of 3.2 less than the nuclear moment of a proton and the number of lines in the case of D should be greater due to the difference in the spins of the H and D nuclei (for H $I = 1/2$ and D $I = 1$). This should lead to smearing of the hyperfine structure, which was actually observed in the experiment.

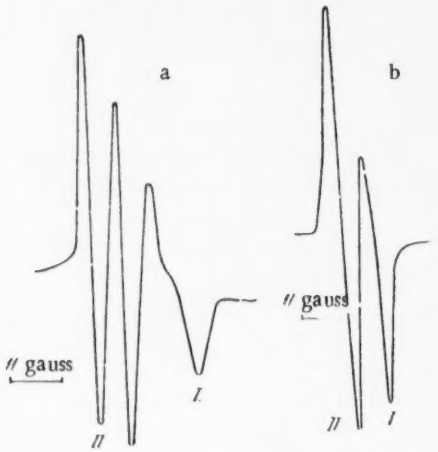
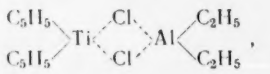


Fig. 2.

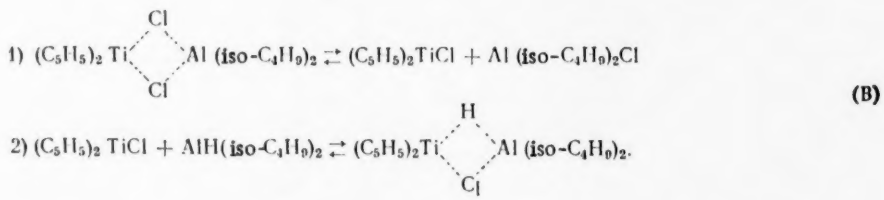
On the basis of these and literature data, some conclusions may be drawn on the structure of the complexes formed.

As a result of x-ray structural analysis, Nata et al., [2] came to the conclusion that the reaction product of $Al(C_2H_5)_3$ and $(C_5H_5)_2TiCl_2$ is a compound with the structure:

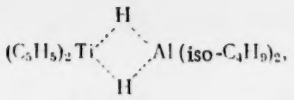

(A)

in which two chlorine atoms play the part of bridging bonds between the titaniun and the aluminum. This compound contains an unpaired electron [3] and apparently corresponds to signal I we observed. A similar compound is evidently obtained by the reaction of $AlH(iso\text{-}C_4H_9)_2$ with $(C_5H_5)_2TiCl_2$ with a component ratio of 1 : 1 as in this case the liberation of hydrogen is observed and the composition of the compound formed, its visible spectrum, and its electron paramagnetic resonance spectrum correspond to compound A.

With further addition of $AlH(iso\text{-}C_4H_9)_2$ there is no liberation of gases, but the electron paramagnetic resonance spectrum and the color of the solution change. This may be explained by the following reactions of complex A:


(B)

Instead of chlorine in the bridging bond, compound B contains hydrogen, the splitting at which leads to the formation of a doublet in signal II. Further replacement by a similar mechanism leads to the formation of a compound with two bridging bonds through H atoms:



(C)

which corresponds to signal III.

The observed displacement of the g value from I to III indicates the extent of the change in character of the orbit containing the unpaired electron. In this change there is apparently an increase in the spin density of the unpaired electron on the aluminum atom.

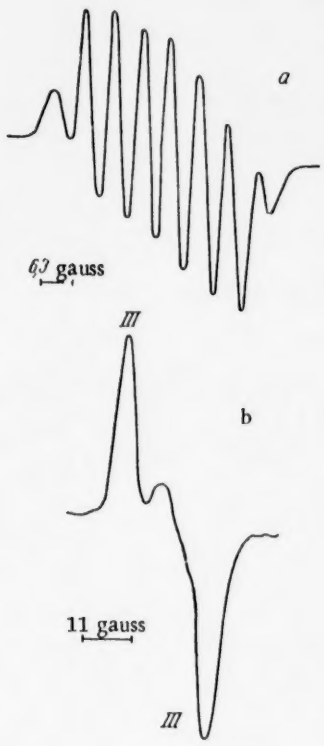


Fig. 3.

Complexes B and C are formed by equilibrium reactions as the addition of excess $Al(C_2H_5)_2Cl$ led to the reverse change of signal III to signal II.

It is possible that similar structures are formed in the case of the insoluble systems $AlR_3 + TiCl_4$ where the lack of a hyperfine structure in the observed electron paramagnetic resonance spectrum [4] made it impossible to draw conclusions on the structure of the complexes.

For these systems it is possible to propose the formation of the structure:

However, in this case compounds of this type play the part of intermediate products as their dissociation to AlR_2Cl and $TiCl_3$, which precipitate, evidently proceeds practically to completion. This is in agreement with the fact that in the system $Al(iso\text{-}C_4H_9)_3 - TiCl_4$ the electron paramagnetic resonance signal, which is visible at room temperature, gradually disappears.

The catalytic activity of the complexes observed was of great interest. We observed that solutions of complexes corresponding to signals I, II, and III polymerized ethylene to form polyethylene. During the polymerization the electron paramagnetic resonance spectra of the solution changed in accordance with the transition III → II → I. A further study of this interesting fact may make it possible to determine the mechanism of the initiation of catalytic polymerization.

EXPERIMENTAL

$Al(CH_3)_3$ was prepared by prolonged boiling of CH_3I with an alloy of Al (40%) and Mg (60%) and subsequent purification of the product by two vacuum distillations (m. p. 15°). $Al(C_6H_5)_3$ and $Al(iso\text{-}C_3H_7)_3$ were prepared through organomercury compounds according to the scheme:

$$RBr \xrightarrow{NaHg} R_2Hg \xrightarrow{Al} R_3Al.$$

The $Al(C_6H_5)_3$ was purified by two recrystallizations from xylene (m. p. 235°). The $Al(iso\text{-}C_3H_7)_3$ was purified by two vacuum distillations (b. p. 40-42°/1 mm). $AlH(iso\text{-}C_4H_9)_2$ and $AlD(iso\text{-}C_4H_8D)_2$ were prepared by heating $Al(iso\text{-}C_4H_9)_3$ and $Al[CH_2CD(CH_3)_2]_3$ at 140° for 2 hr while the isobutylene formed was pumped off; the products were purified by two vacuum distillations (b. p. 118°/1 mm). $(C_5H_5)_2TiCl_2$ was prepared according to the scheme

$$C_5H_6 \xrightarrow{Na} NaC_5H_5 \xrightarrow{TiCl_4} TiR_2Cl_2$$

and purified by recrystallization from chloroform and toluene. Diethylaluminum chloride was obtained by the reaction

$$2AlR_3 + AlCl_3 \rightarrow 3AlR_2Cl$$

and purified by vacuum distillation (b. p. 96°/1 mm).

Experimental procedure. All operations with alkylaluminums were carried out in a special cell in an atmosphere of argon, free from traces of moisture and oxygen.

The absorption spectrum of the components in the visible region was plotted on an SF-4 spectrophotometer. The electron paramagnetic resonance spectra were plotted on an ÉPR-2 IKhF spectrometer with high-frequency modulation of the magnetic field.

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EFFECT OF THE TIME FACTOR ON THE CHARACTER OF THE COMPOSITION – HEAT-RESISTANCE DIAGRAM OF ALLOYS OF THE FIVE-COMPONENT SYSTEM Ni – Cr – W – Ti – Al

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Nickel is capable of forming solid solutions and metallic compounds with many elements. Due to the absence of polymorphism, crystallochemical reactions in nickel alloys consist merely of the formation of Kurnakov compounds from solid solutions and conversions of supersaturated solid solutions. With many metals (Cr, Mo, W, V, Nb, Ti, Al, Be, etc.), nickel forms limited solid solutions with a temperature dependent solubility. The solubility of the components in nickel usually falls with a fall in temperature. This creates favorable conditions for the formation of nickel solid solutions of both simple and complex composition in a supersaturated state and successive processes of the formation of extra phases and dispersion hardening.

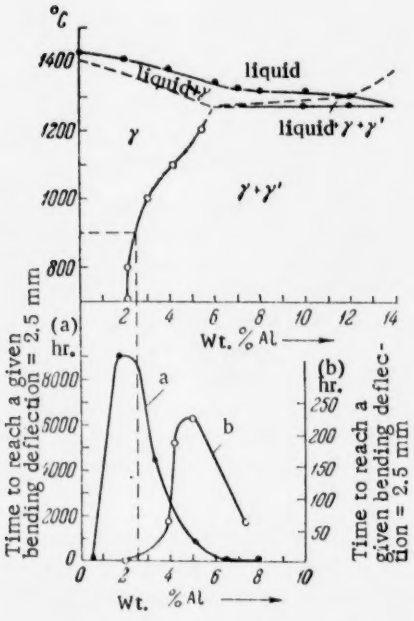

Fig. 1. Phase diagram and composition–heat-resistance diagram of alloys from one cross section of the five-component system Ni–Cr–W–Ti–Al at 900°C.

The work of many investigators [1-8] has been devoted to the study of the effect of the duration of crystallochemical reactions on the heat resistance of nickel alloys.

Most authors have examined the effect of the duration of crystallochemical reactions on the change in heat resistance of an alloy of a single composition. It seemed interesting to investigate simultaneously the effect of composition and conversion time on the heat resistance of alloys of metallic systems. To solve this problem we studied the creep of alloys from one of the cross sections of the five-component system Ni–Cr–Ti–Al with a variable Al content from 0 to 7.9% (calculated on the Ni content) and with constant Cr, W, and Ti contents.

The phase diagram of the section studied is given in Fig. 1.

Before creep tests, the samples were given the following heat treatment: heating to 1150°C, kept at this temperature for 7 hr, and cooling in air. After this type of homogenization, alloys containing up to 5.1% of aluminum showed the structure

of five-component solid solutions with a small amount of extra phase γ', liberated as a result of the cooling in air. Above this aluminum content, there appeared a eutectic, consisting of the solid solution γ and the phase γ'.

Creep testing of alloys of this cross section was carried out by the centrifugal method on 3-4 parallel samples. The temperature was kept at 900° and the initial stress was 6 kg/mm^2.

As the investigation showed, for a number of compositions the stress chosen made it possible to study the deformation of the alloy over the long period of 10,000 and more hours. Up to the present time, testing has been carried out for 10,000 hours and will be continued for up to 25,000 and more hours.

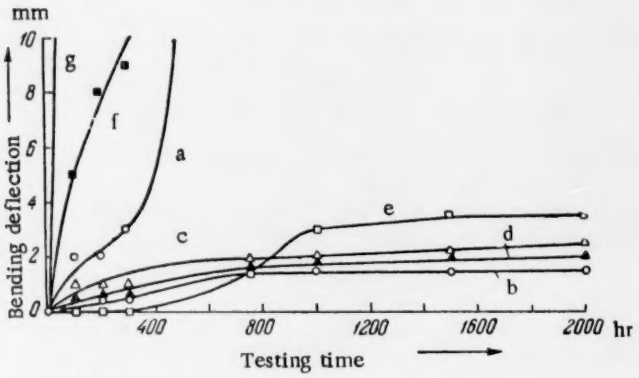

Fig. 2. Creep curves for alloys of the system Ni–Cr–W–Ti–Al over 2000 hr.

As a characteristic of creep we used the value of the bending deflection of samples during deformation.

For more detailed analysis of the curves of creep against deformation time and composition we show them on diagrams, one of which (Fig. 2) gives more details of the creep process for alloys of various compositions up to 2000 hr deformation and the second (with a smaller time scale) (Fig. 3), up to 10,000 hr deformation.

An examination of the curves in Fig. 2 shows that alloys with a high aluminum content (6.5 and 7.9%), whose compositions lay within the region of cocrystallization of the γ-solid solution and the eutectic, were not heat resistant. They were deformed rapidly under these conditions: the alloy with 7.9% of Al (curve g, Figs. 2 and 3) was tested for up to 500 hr and a bending deflection of 60 mm, while the alloy with 6.5% Al was tested for up to 2500 hr with a bending deflection of 59 mm (curve f, Figs. 2 and 3). A high rate of deformation was shown by the alloy with 0.5% Al, which was tested for up to 750 hr with a bending deflection of 60 mm and which corresponded to a dilute solid solution (curve a, Figs. 2 and 3). The creep curves of these three alloys were characterized by a rapid increase in bending deflection with time. The alloys lying in the region of concentrated and supersaturated solid solutions (from 1.8 to 5.1% Al) had a high heat resistance, differing sharply from the first two compositions, which were heterogeneous alloys with a eutectic component, and the third composition, which was a dilute solid solution.

It is extremely indicative that in the initial stage (up to 300-400 hr) the alloy with 5.1% Al (maximum supersaturation) was hardly deformed (curve e, Fig. 2). During this period of testing, the alloy of this composition evidently could only have undergone the first stage of dispersion decomposition of the supersaturated solid solution with maximum hardening of the latter. After 300-400 hr, this alloy underwent rapid creep, which apparently corresponded to the beginning of the coagulation process in the decomposition of the solid solution.

During the period from 400 to 1000 hr, the greatest creep rate was observed and in this period the bending deflection changed from almost zero to 3.5 mm. Under these conditions, alloys with an aluminum content of 1.8 (b), 2.8 (c), and 3.4% (d) were deformed rapidly in the initial stage over the first 100-200 hr and then at a steady low rate right up to 2000 hr.

Thus, in accordance with these curves it may be considered that over a small deformation period (up to 300-400 hr), the alloy with maximum supersaturation (with 5.1% Al) is the most heat-resistant one, while with an increase in the time above 700-800 hr, the most heat-resistant alloys were those with a lower degree of supersaturation (3.4, 2.8, and 1.8% Al), lying close to the limiting solubility of Al. Of the last three compositions, the alloy with 1.8% Al had a purely polyhedral microstructure and showed the lowest creep rate.

A further increase in the creep testing time to 10,000 hr did not alter the general character of the change in the creep curves for alloys of different compositions, with the exception of the two compositions with 2.8 and 3.4% of Al.

In this case also (see Fig. 3), the alloy with 5.1% Al (curve e) showed a high bending deflection and the least was shown by the alloy with 1.8% Al (curve b). It is most interesting that the alloys with Al contents of 2.8% (curve c) and 3.4% (d) had bending deflections intermediate between those of alloys with 5.1% and 1.8% of Al during the whole testing time, but after 5000 hr the bending deflection of the alloy with 3.4% Al became greater than that of the alloy with 2.8% Al. The alloy with 2.8% Al was a less supersaturated solid solution than the alloy with 3.4% Al. In this case, as a result of the higher supersaturation in the alloy with 3.4% Al, coagulation of the extra phase proceeded more rapidly, producing an acceleration of creep.

A composition–heat-resistance diagram for 900° and a stress of 6 kg/mm^2 (see Fig. 1, curve a) was constructed for a given bending deflection (equal to 2.5 mm) of alloy samples after a deformation time of 10,000 hr.

It showed that the maximum time to reach this deflection (or the maximum heat resistance) was shown by alloys containing 1.8-2.8% Al and lying close to limiting saturation with an almost homogeneous solid solution structure or with a slight degree of heterogeneity. As the degree of supersaturation of the solid solution increased (alloys with 3.4 and 5.1% of Al) and there was strong heterogeneity of structure with the formation of eutectic mixtures, the heat resistance of the alloys successively and considerable decreased. Dilute solid solutions (alloy with 0.5% of Al) also showed a low heat resistance. If this composition–heat-resistance diagram is compared with that which we obtained previously for alloys of this system with a comparatively short testing time (up to 200-300

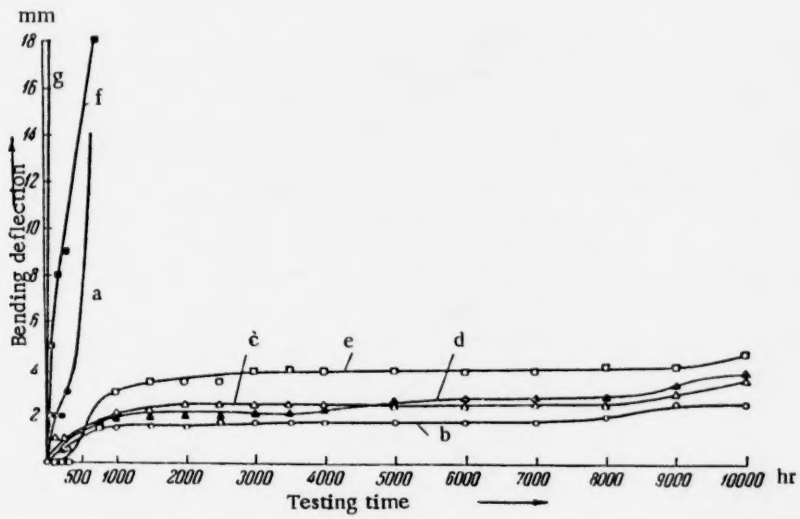

Fig. 3. Creep curves of alloys of the system Ni–Cr–W–Ti–Al over 10,000 hr.

hr), but with a high stress, a substantial difference appears. It consists of a considerable displacement to the right of the position of the heat-resistance maximum on the composition–heat-resistance diagram obtained by heat-resistance testing for short periods. Figure 1b shows a diagram for a deformation time of 250 hr at 900° and a stress of 8 kg/mm^2. This figure shows that the heat-resistance maximum corresponded to the composition of alloys containing 4.5-5.5% Al, i.e., the composition of alloys with the maximum degree of supersaturation of the solid solution.

In this case, lower heat-resistance values were obtained both in the region of dilute solid solutions and for alloys whose structure consisted of a solid solution with a eutectic.

An explanation for this type of displacement of the region of maximum heat resistance of alloys on composition–heat-resistance diagrams for short-term (of the order of hundreds of hours) and prolonged (up to 10,000 hr) testing should be sought in the effect of the of the time factor on the physicochemical conversions and changes in structure of the alloys during the testing.

Under conditions of short-term heat-resistance testing, alloys with maximum supersaturation have the greatest resistance due to the higher internal stresses in the solid solution lattice. The first stage in the decomposition of such supersaturated solid solutions, producing only the formation of atomic groupings rich in components and the liberation of an extra phase in a finely dispersed state, guarantees the retention of the hardened state of the alloy over this comparatively short time. This hardening effect becomes less in the region of less supersaturated solutions and in the region of the formation of eutectic mixtures during crystallization. It is absent with dilute solid solutions. Due to the different effect of the time factor, in connection with the different character of the crystallochemical reaction, in prolonged creep testing processes the hardening factor is changed into the reverse. The hardening process is replaced by softening of the alloys. This softening proceeds more rapidly with time, the higher the degree of supersaturation of the solid solution and the longer the testing time. Diffusion processes occur to a considerable extent in the latter case. The formation of an extra phase with its subsequent coagulation leads to a fall in heat resistance. Thus, the heat-resistance maxima for prolonged testing are displaced into the region of less supersaturated solid solutions, which have a higher thermal stability and a lower tendency for decomposition and coagulation of the extra phase during the prolonged action of a stress.

The present investigation showed that the heat-resistance maxima on isothermal composition–heat-resistance diagrams may move, depending not only on the temperature factor, as was established previously [9], but also the time factor.

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POTENTIOMETRIC METHOD OF TITRATING ACIDS WITH QUATERNARY AMMONIUM BASES

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The analysis of weak and very weak acids and mixtures of them presents very great difficulties. These difficulties can be overcome readily by titration of the acids in nonaqueous solutions [1, 2]. The advantages of titration in nonaqueous media have been demonstrated quite well in the literature [3]. At the present time, methods of titrating various substances in nonaqueous media find wide application in scientific research and factory laboratories [4-6].

We developed a potentiometric method of titrating strong, weak, and very weak acids in nonaqueous media, which made it possible to determine not only individual acids, but also their binary and polycomponent mixtures. A clear example of the sort of results which may be obtained by using the method of differential determination of acids in nonaqueous solutions is the titration of five-component mixtures of acids, for example, perchloric, hydrochloric, trichloroacetic, and acetic acids and β-naphthol.

EXPERIMENTAL

For our investigation we used various acids and mixtures of them; 1) very weak acids, whose dissociation constants are so low that it is impossible to titrate them in an aqueous medium; 2) water-insoluble acids which can be titrated only in nonaqueous solvents; 3) mixtures of weak and very weak acids whose differential titration cannot be achieved in aqueous solution due to the leveling effect of water.

TABLE 1

Results of Quantitative Determination of Some Individual Acids

Substance determined	Amount taken, g	Amount found, g	Relative error, %
α-Naphthol	0,0303	0,0308	+1,7
β-Naphthol	0,0205	0,0209	+1,9
Palmitic acid	0,1101	0,1114	+1,1
Stearic acid	0,0493	0,0496	+0,5
Oleic acid	0,1697	0,1715	+1,0
o-Nitrophenol	0,0432	0,0439	+1,6
p-Nitrophenol	0,0528	0,0532	+0,7
2,4-Dinitrophenol	0,0371	0,0370	−0,3
2,5-Dinitrophenol	0,0169	0,0169	0,0
2,6-Dinitrophenol	0,0531	0,0527	−0,8
2,4,6-Trinitrophenol	0,0635	0,0633	−0,3

It was found that the best differentiating solvents for the determination of weak and very weak acids and mixtures of them are ketones and, in particular, methyl ethyl ketone. As the titrant we used a benzene–methanol solution of tetraethylammonium hydroxide (5:1), whose titer was established against chemically pure benzoic acid. The titration was carried out in a stream of nitrogen and the potential was measured on an LP-5 potentiometer with glass and calomel electrodes.

Titration of very weak acids. As examples of weak and very weak organic acids, we titrated phenol, m-, o-, and p-cresols, thymol, hydroquinone, resorcinol, pyrogallol, α- and β-naphthols, etc. These compounds are very weak acids (pK ~10) and therefore it is impossible to determine the equivalence point during their titration in an aqueous

medium. These compounds become stronger acids in methyl ethyl ketone and may be titrated with tetraethylammonium hydroxide (Fig. 1). Examination of the titration curves shows that potentiometric titration in a nonaqueous medium may be used successfully for the determination of very weak acids, including phenols. The determination error was ± 2% (Table 1).

Titration of water-insoluble organic acids. Some organic compounds, forming homologous series of saturated and unsaturated monobasic acids, were titrated. As Fig. 1 shows (curves 3, 4, and 5), saturated (like stearic) and unsaturated (like oleic) acids are quite strong acids in methyl ethyl ketone. An examination of the curves shows that potentiometric titration in nonaqueous media can be used for quantitative determination of these compounds. The determination error was ±1% (Table 1).

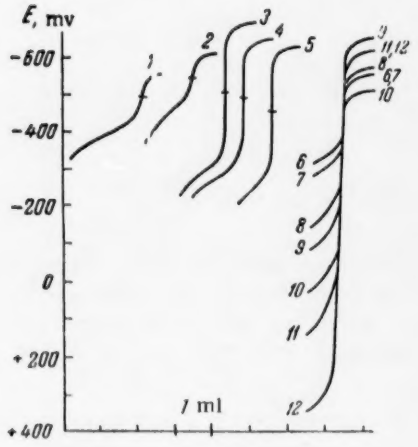

Fig. 1. Potentiometric titration curves of individual acids by tetraethylammonium hydroxide in methyl ethyl ketone: 1) α-naphthol; 2) β-naphthol; 3) palmitic acid; 4) stearic acid; 5) oleic acid; 6) o-nitrophenol; 7) m-nitrophenol; 8) p-nitrophenol; 9) 2,4-dinitrophenol; 10) 2,6-dinitrophenol; 11) 2,5-dinitrophenol; 12) 2,4,6-trinitrophenol.

Differential titration of mixtures of acids. To determine the possibility of differential titration of acids, it was first necessary to obtain the titration curves of the individual compounds. By comparison of the titration curves of the separate acids with those of their mixtures we could determine whether differential titration was possible (if the beginning of the titration jumps of the individual acids differed by more than 100 mv). Figure 2 shows titration curves of mixtures of acids. Examination of the titration curves shows that in methyl ethyl ketone dinitrophenols are stronger acids then nitrophenols and trinitrophenol is a stronger acid than dinitrophenols (Fig. 1). As the beginnings of the titration jumps of the individual phenols differ by more than 100 mv, mono-, di-, and trinitrophenols may be titrated differentially in binary and tricomponent mixtures. The results of quantitative analysis of mixtures of acids are given in Table 2.

The data obtained show that the error in the determination of individual components in binary and ternary mixtures lies within the limits of ±2%.

Thus, the data we obtained show that tetraethylammonium hydroxide in a methyl ethyl ketone medium may be used for rapid titration of strong, weak, and very weak acids and their mixtures with sufficient accuracy for quantitative determination.

TABLE 2

Results of Quantitative Determination of Mixtures of Acids

Substance determined	Amount taken, g	Amount found, g	Relative error, %	Substance determined	Amount taken, g	Amount found, g	Relative error, %
2,4,6-Trinitrophenol	0,0519	0,0521	+0,4	2,4-Dinitrophenol	0,0326	0,0320	—1,9
2,5-Dinitrophenol	0,0176	0,0174	—1,1	o-Nitrophenol	0,0545	0,0551	+1,2
2,4,6-Trinitrophenol	0,0403	0,0400	—0,7	2,4,6-Trinitrophenol	0,0468	0,0463	—1,1
p-Nitrophenol	0,0594	0,0591	—0,5	2,4-Dinitrophenol	0,0406	0,0398	—2,0
2,4,6-Trinitrophenol	0,0529	0,0521	—1,5	p-Nitrophenol	0,0645	0,0657	+1,8
o-Nitrophenol	0,0591	0,0584	—1,2	2,4,6-Trinitrophenol	0,0605	0,0600	—0,8
2,6-Dinitrophenol	0,0353	0,0350	—0,9	2,6-Dinitrophenol	0,0336	0,0332	—1,5
o-Nitrophenol	0,0385	0,0388	—0,9	o-Nitrophenol	0,0765	0,0779	+1,9

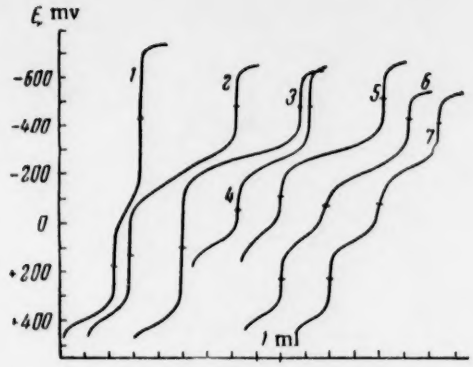

Fig. 2. Potentiometric titration curves of polycomponent mixtures of strong, weak, and very weak acids by tetraethylammonium hydroxide in methyl ethyl ketone: 1) 2,4,6-trinitrophenyl + 2,5-dinitrophenol; 2) 2,4,6-trinitrophenol + p-nitrophenol; 3) 2,4,6-trinitrophenol + + o-nitrophenol; 4) 2,6-dinitrophenol + o-nitrophenol; 5) 2,4-dinitrophenol + o-nitrophenol; 6) 2,4,6-trinitrophenol + 2,4-dinitrophenol + p-nitrophenol; 7) 2,4,6-trinitrophenol + 2,6-dinitrophenol + o-nitrophenol.

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*Original Russian pagination. See C. B. translation.

PREPARATION OF BIFERROCENYL BY THE ULLMANN REACTION

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In [1] we described the synthesis of biferrocenyl from diferrocenylmercury by heating the latter with palladium black. The main product of this reaction was ferrocene and biferrocenyl was formed in a yield of only 6% of theoretical. At the same time as we, Goldberg and Mayo [2] obtained biferrocenyl by the reaction of lithio- and dilithioferrocene with tri-n-hexylbromosilane. The biferrocenyl yield was not reported, but apparently it was also low.

In the present work we showed that biferrocenyl is obtained in 75-80% of theoretical yield by heating iodoferrocene with Gattermann copper, when only small amounts of ferrocene are formed as a by-product.

$$2C_5H_5FeC_5H_4I \xrightarrow{Cu} C_5H_5FeC_5H_4 — C_5H_4Fe\,C_5H_5.$$

We previously [3] showed that the iodine of iodoferrocene is inert to nucleophilic substitution reactions with such reagents as sodium methylate and potassium acetate in an alcohol medium.* When copper is added as a catalyst, ferrocene is the main reaction product. It is probable that copper catalyzes homolytic cleavage of iodoferrocene and the ferrocenyl radical thus formed abstracts hydrogen from the solvent, while in the absence of the latter it dimerizes and abstracts hydrogen from a ferrocenyl nucleus only to a very small extent to form ferrocene.

EXPERIMENTAL

Preparation of iodoferrocene [3]. A hot solution of 30 g (0.12 mole) of iodine in 100 ml of xylene was added with vigorous stirring to a suspension of 10 g (0.023 mole) of carefully ground chloromercuriferrocene in 100 ml of xylene, heated almost to boiling with stirring. Stirring was continued until the mixture cooled to room temperature. The precipitate was collected, washed with xylene and hot alcohol, ground in a mortar, and stirred vigorously for 1.5 hr with 20-25 ml of a saturated solution of sodium thiosulfate. The precipitate was then collected on a filter, extracted several times with ether, stirred again with sodium thiosulfate solution for 45 min, and then collected on a filter again and extracted several times with ether. The ether extracts, which contained iodoferrocene, were combined and dried with magnesium sulfate. The ether was removed. The iodoferrocene was recrystallized from methyl alcohol (precipitated on cooling to −10°). The m. p. was 44-45°. The yield was 4.7 g (64 % of theoretical).

Preparation of biferrocenyl. Iodoferrocene (0.58 g) in an open test tube was placed in a glycerol bath, heated to 100°. When the iodoferrocene had melted, 0.4 g of freshly prepared Gattermann copper was added, whereupon the temperature in the test tube rose to 120° and the reaction mixture solidified. The temperature of the bath was then raised to 150° for 15 min and then the reaction mixture was cooled in air, ground in a mortar, and extracted with ligroin. The solution was chromatographed on an alumina column. The ligroin

*As A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd [4] showed, the halogen of haloferrocenes exchanges under quite mild conditions under the action of copper salts.

eluted 0.01 g of ferrocene (3% yield). The m. p. and the m. p. of a mixture with an authentic sample were 172-173°. A mixture of benzene and ligroin (in a ratio of 2:1) eluted biferrocenyl, which was identical with that which we obtained previously [1] both in m. p. and infrared spectrum. The yield was 0.26 g (79% of theoretical). The m. p. of biferrocenyl and the m. p. of a mixture with an authentic sample were 228-230° (with decomp.).

Heating iodoferrocene in methanol in the presence of copper. A mixture of 0.2 g of iodoferrocene, 0.1 g of freshly prepared Gattermann copper, and 4 ml of methyl alcohol was heated in a sealed tube for 12 hr at 120°. The reaction mixture was then poured into water. The precipitated ferrocene was collected and recrystallized from ethyl alcohol. The m. p. and the m. p. of a mixture with an authentic sample of ferrocene were 172-173°.

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ADDITION OF LITHIUM DIALKYLPHOSPHIDES TO VINYLACETYLENES

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It was previously established that lithium dialkylamides add to vinylacetylenes and treatment of the adducts with water forms allene or acetylene amines [1].

To determine the behavior of other compounds of the type R_2E-Li, where E is a Group V element, we studied under the same conditions the reaction of vinylacetylene and two of its homologs, vinylmethyl- and vinylethylacetylenes, with lithium diethyl- and dibutylphosphides.

Lithium dialkylphosphides were prepared for the first time in 1959 by the action of phenyllithium on dialkylphosphines [2]. Of the reactions of these compounds, only the interaction with aromatic ketones has been described [3].

As a result of the addition of lithium dialkylphosphides to vinylacetylenes one could expect the formation of acetylene, allene, or 1,3-diene tertiary phosphines. As in all the cases investigated up to the present time the radical has always added to the terminal atom of the conjugated system in the reactions of vinylacetylenes with alkylylithiums [4] and lithium amides [1], phosphines with a normal structure (I), (II), and (III, where R = H) were most probable.

$$R-C\equiv C-CH_2-CH_2-PR'_2, \quad \text{(I)}$$

$$R-CH=C=CH-CH_2-PR'_2, \quad \text{(II)}$$

$$R-CH=CH-CH=CH-PR'_2. \quad \text{(III)}$$

In actual fact the addition of lithium phosphides to vinylacetylene proceeded in all three possible directions, while in the case of vinylmethyl- and vinylethylacetylenes, we obtained exclusively or almost exclusively allene tertiary phosphines (II).

The tertiary phosphine obtained by water treatment of the adduct of lithium dibutylphosphide and vinylacetylene undoubtedly contained 1-dibutylphosphino-3-butyne (I, R = H). Its infrared spectrum contained the characteristic frequencies of a terminal acetylene grouping (2120 and 3318 cm^{-1}), together with the frequencies of allene (1960 and 905 cm^{-1}) and 1,3-diene (1560-1600 and 3083 cm^{-1}) groupings. About 40% of acetylene (I) was detected in it by the usual determination [5]. However, the substance was not a pure phosphine.

The acetylene phosphine (I, R = H) could have been formed as a result of 3,4-addition of the lithium dialkylphosphide (at the double bond) or as a result of isomerization of the allene adduct (II, R = H). It is also possible that the lithium dialkylphosphide was added not to free vinylacetylene, but to the lithium acetylide. In this case the addition of a second lithium atom to the same carbon atom is improbable.

The infrared spectra of the tertiary phosphines obtained from vinlymethyl- and vinylethylacetylenes in about 35% yield contained intense frequencies characteristic of the allene grouping (about 1960 and 870 cm^{-1},

curves 2 and 4). The frequencies of the acetylene bond were completely absent from the spectra and the frequencies of a conjugated system of double bonds were either absent or extremely weak and doubtful. Most likely they belonged to phosphines of type (III), formed as a result of isomerization of adducts of type (II).

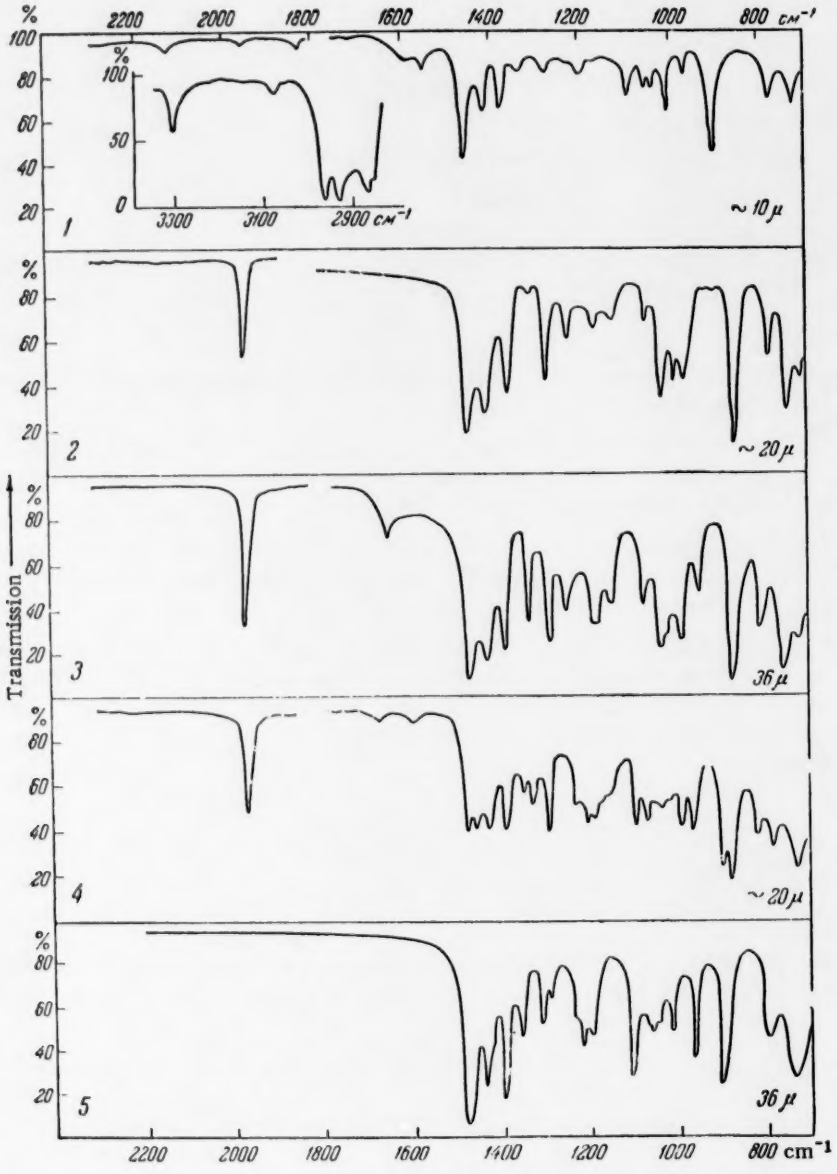

Fig. 1. Infrared transmission spectra: 1) Phosphine from vinylacetylene; 2) 1-diethylphosphino-2,3-pentadiene; 3) 1-diethylphosphino-2,3-hexadiene; 4) 1-dibutylphosphino-2,3-hexadiene; 5) tributylphosphine.

Attention is attracted by the fact that vinylmethyl- and vinylethylacetylenes behaved identically in the reaction with lithium phosphides. Meanwhile the action of lithium dialkylamides on vinylethylacetylene also gave allene adducts, while on vinylmethylacetylene, largely the dimer and polymers.

Considerable amounts of high-boiling products containing phosphorus were formed in all cases together with the tertiary phosphines. We did not study them in detail, but we consider that they are higher telomers of the phosphines we isolated. We observed similar telomerization in the reaction of amines with vinylacetylene [1].

During the investigation it was established that lithium dialkylphosphides react readily with halogen derivatives to form saturated tertiary phosphines. This reaction has not been carried out previously with lithium dialkylphosphides, but it is known that lithium phosphide reacts readily with halogen derivatives to form primary phosphines [6]. By the action of lithium diethylphosphide on butyl chloride we obtained diethylbutylphosphine and similarly, from lithium dibutylphosphide and butyl chloride, tributylphosphine was obtained.

This property of lithium dialkylphosphides compelled us to take special precautions so that no unreacted alkyl chloride remained in the preparation of alkyllithiums, which we used for the synthesis of lithium dialkylphosphides.

Phosphines with an allene grouping are described for the first time. The literature contains few data on the chemistry of unsaturated phosphines in general. Trivinyl- and triallylphosphines, for example, are known and also phosphines with unsaturated or aryl and allyl radicals [7-9]. They were all obtained from chlorine compounds of phosphorus and organometallic compounds. There are also few literature data on the addition of phosphines and phosphites to unsaturated hydrocarbons.

The allene tertiary phosphines we obtained were quite mobile, colorless liquids with the characteristic smell of phosphines. Exaltation of the molecular refraction was observed. In air they were rapidly oxidized and formed tars, acquiring a brown color, but they could be stored in an argon atmosphere for a long time without change. They could not be hydrogenated over palladium.

EXPERIMENTAL

Lithium dialkylphosphides were prepared by the reaction of equivalent amounts of butyllithium [13] and dialkylphosphines in ether. The dialkylphosphines were obtained by lithium aluminum hydride reduction of the reaction products of phosphorus thiochloride and alkylmagnesium bromides [14]. In contrast to the directions in [12], we did not isolate the reaction product of phosphorus thiochloride and butylmagnesium bromide, but reduced the whole reaction mixture after decomposition of the organomagnesium complex with water and drying the reaction mixture over $CaCl_2$.

A solution of dialkylphosphine (0.08 mole in 25 ml of ether) was added with mechanical stirring to 75 ml of an ether solution of butyllithium (0.08-0.1 mole) and after 30 min, the appropriate hydrocarbon (0.08 mole) was added dropwise to the solution obtained. Heat was evolved and the mixture became yellow. After being stirred for 30 min, the mixture was poured into ice water. The ether solution of phosphines was separated from the aqueous layer, dried, and distilled. The phosphines usually distilled over narrow ranges (1°). All the work was carried out in an argon atmosphere.

Addition of lithium dibutylphosphide to vinylacetylene. From the amounts of reagents given above we obtained 1.6 g (10%) of phosphine and 2.5 g of polymers. The phosphine was 1-dibutylphosphino-3-butyne with impurities. It had b. p. 95-96°/5 mm, d_4^{20} 0.8448; n_D^{20} 1.4830.

Found %: C 73.85; 73.92; H 12.17; 12.08; P 13.20. $C_{12}H_{23}P$. Calculated %: C 72.68; H 11.69; P 15.62.

Infrared spectrum: 725 av., 738 av., 905 s., 966 w., 1005 av., 1035 w., 1052 w., 1094 w., 1200 w., 1281 w., 1339 w., 1376 av., 1415 av., 1460 s., 1563-1600 w., 1816 w., 1960 v.w., 2120 w., 2860 v.s., 2873 v.s., 2927 v.s., 2957 v.s., 3083 w., 3318 s. cm^{-1}.

Addition of lithium diethylphosphide to vinylmethylacetylene. We obtained 4.5 g of phosphine and 4.5 g of residue. The phosphine was 1-diethylphosphino-2,3-pentadiene. It had b. p. 60-61°/5 mm, d_4^{20} 0.8697; n_D^{20} 1.5050. MR found 54.01; calculated 53.07.

Found %: C 69.50; 69.05; H 11.16; 10.98; P 19.49; 19.22; $C_9H_{17}P$. Calculated %: C 69.20; H 10.97; P 19.83.

Infrared spectrum: 720 s., 745 s., 786 av., 862 v.s., 975 s., 997 s., 1025 s., 1060 w., 1134 w., 1180 w., 1234 av., 1281 s., 1368 s., 1415 s., 1455 v.s., 1965 s. cm^{-1}.

Addition of lithium diethylphosphide to vinylethylacetylene. We obtained 4.6 g of phosphine and 7.3 g of residue. The phosphine was 1-diethylphosphino-2,3-hexadiene. It had b. p. 78-79°/5 mm, d_4^{20} 0.8569, n_D^{20} 1.5025. MR found 58.78; calculated 57.69.

Found %: C 70.74; 70.30; H 11.23; 11.34; P 18.10; 17.95. $C_{10}H_{19}P$. Calculated %: C 70.55; H 11.25; P 18.20.

Infrared spectrum: 730 av., 763 s., 818 av., 855 w., 876 v.s., 950 w., 993 w., 1036 av., 1067 av., 1140 w., 1185 av., 1240 av., 1282 av., 1325 av., 1378 av., 1414 av., 1458 v.s., 1648 w., 1955 s. cm^{-1}.

Addition of lithium dibutylphosphide to vinylethylacetylene. We obtained 5 g of phosphine and 7.5 g of residue. The phosphine was 1-dibutylphosphino-2,3-hexadiene. It had b. p. 125-126°/5 mm, d_4^{20} 0.8534; n_D^{20} 1.4952. MR found 77.38; calculated 76.16.

Found %: C 73.88; 74.69; H 11.96; 12.39; P 13.24; 13.06. $C_{14}H_{27}P$. Calculated %: C 74.29; H 12.02; P 13.69.

Infrared spectrum: 724 v.s., 782 s., 818 s., 876 v.s., 895 s., 965 s., 987 s., 1019 w., 1037 av., 1065 av., 1091 av., 1139 w., 1180 av., 1198 av., 1225 w., 1278 s., 1324 av., 1340 w., 1378 s., 1410 s., 1445 s., 1465 s., 1648 w., 1955 s. cm^{-1}.

Preparation of trialkylphosphines. The action of an ether solution of butyl chloride on an ether solution of lithium diethylphosphide gave a 60% yield of diethylbutylphosphine. It had b. p. 41-42°/5 mm, 106-107°/100 mm, d_4^{20} 0.8094; n_D^{20} 1.4600, which agrees with literature data [15]. Tributylphosphine was obtained analogously. It had b. p. 146-147°/50 mm, d_4^{20} 0.8191; n_D^{20} 1.4632, which also agress with literature data [16].

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REACTION OF SILICON HYDRIDES WITH α- AND β-CHLORONAPHTHALENES AND p-DICHLOROBENZENE: PYROLYSIS OF ETHYLCHLOROSILANES IN THE PRESENCE OF ARYL CHLORIDES

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We recently showed [1, 2] that the reaction of aryl chlorides with silicon hydrides in the vapor phase at high temperatures according to the scheme:

$$RCl + HSiR'_nCl_{3-n} \rightarrow RR'_nSiCl_{3-n} + HCl \quad (I)$$

(where R is an aromatic radical, R' is an alkyl or aryl radical, and n = 0, 1, or 2) is a general method for the synthesis of arylchlorosilanes.

A. D. Petrov, V. A. Ponomarenko, and G. Odabashyan used such silicon hydrides as dichlorosilane [3] and methylchlorosilane [4] in this reaction and this made it possible to synthesize phenyldichlorosilane and methylphenylchlorosilane together with other substances. British investigators obtained good yields of various trifluoromethylphenylchlorosilanes by this method [5].

In the present investigation the high-temperature condensation of silicon hydrides with α- and β-chloronaphthalenes was studied in detail. In addition, it was established for the first time that it is possible to form p-bis-(trichlorosilyl)-benzene and its analogs by scheme A and also phenyldichlorosilane from ethyldichlorosilane and chlorobenzene according to scheme B:

$$p\text{-}ClC_6H_4Cl + HSiCl_3 \rightarrow p\text{-}ClC_6H_4SiCl_3 + p\text{-}Cl_3SiC_6H_4SiCl_3; \quad (A)$$

$$C_2H_5HSiCl_2 \rightarrow C_2H_4 + [H_2SiCl_2] \xrightarrow{C_6H_5Cl} C_6H_5SiCl_2H. \quad (B)$$

For α-chloronaphthalene we investigated the effect of the temperature in the reaction zone of the degree of conversion of the silicon hydride and the yields of reaction products. The data obtained are given in Figs. 1 and 2 (τ = 30 sec).

In the case of chloronaphthalenes, as with other aryl chlorides, together with the main reaction, namely, the formation of naphthylchlorosilanes, there was the parallel formation of naphthalene and silicon tetrachloride (or methyltrichlorosilane):

$$C_{10}H_7Cl + HSiR'_nCl_{3-n} \rightarrow C_{10}H_8 + R'_nSiCl_{4-n}. \quad (II)$$

It should be noted that the reaction of silicon hydrides with chloronaphthalenes began at a lower temperature than with chlorobenzene and, as can be seen from Table 1, in this case reaction I predominates over reaction II.

TABLE 1

Starting materials		Substances obtained				Physical properties of chlorosilane obtained				Elementary analysis of arylchlorosilane							
										calculated, %				found, %			
aryl chloride	silicon hydride	$SiCl_4$, CH_3SiCl_3	yield, %	$ArSiCl_3$ or $ArSiCH_3Cl_2$	yield, %	m.p., °C	b. p., °C/mm	n_D^{20}	d_4^{20}	C	H	Si	Cl	C	H	Si	Cl
α-$C_{10}H_7Cl$	$HSiCl_3$	$SiCl_4$	12	α-$C_{10}H_7SiCl_3$	60	54—55	126—127/1	—	—	45,98	2,67	10,82	40,73	46,07 46,00	3,23 3,15	10,80 10,92	39,83 39,20
α-$C_{10}H_7Cl$	CH_3SiHCl_2	CH_3SiCl_3	32	α-$C_{10}H_7SiCH_3Cl_2$	52	—	128—129/1	1,6074	1,2832	54,77	4,24	11,63	29,46	**54,47** 54,58	**4,28** 4,20	**11,82** 11,73	29,34 29,00
β-$C_{10}H_7Cl$	$HSiCl_3$	$SiCl_4$	13	β-$C_{10}H_7SiCl_3$	51	51—52	183—185/1	—	—	45,98	2,67	10,82	40,73	46,12 46,10	3,13 2,98	10,67 10,80	39,24 39,48
β-$C_{10}H_7Cl$	CH_3SiHCl_2	CH_3SiCl_3	33	β-$C_{10}H_7SiCH_3Cl_2$	41	37—38	126—128/1	—	—	54,77	4,24	11,63	29,46	—	—	—	29,34 29,18
p-ClC_6H_4Cl + + C_6H_6	$HSiCl_3$*	$SiCl_4$	18	p-$ClC_6H_4SiCl_3$	29	—	102—104/4	1,5408	1,4258	30,27	1,62	11,38	55,83	30,27 30,25	1,88 1,80	11,95 11,80	55,45 55,00
				p-$(Cl_3Si)_2C_6H_4$	4	76—77	114—115/2	—	—	—	—	—	61,74	—	—	—	61,38 61,52
p-ClC_6H_4Cl + + C_6H_6	$HSiCl_3$**	$SiCl_4$	14	$C_6H_5SiCl_3$	12	—	—	—	—	—	—	—	—	—	—	—	—
				p-$ClC_6H_4SiCl_3$	30	—	101—103/4	1,5400	1,4250	—	—	—	—	—	—	—	—
				p-$(Cl_3Si)_2C_6H_4$	15	76—77	115—117/2	—	—	—	—	—	—	—	—	—	—
p-ClC_6H_4Cl + + C_6H_6	CH_3SiHCl_2*	CH_3SiCl_3	35	p-$ClC_6H_4SiCl_2CH_3$	20	—	81—83/2	1,5345	1,2854	37,25	3,12	12,69	46,94	37,38 37,43	3,44 3,35	12,34 12,20	45,90 46,24
				p-$(Cl_2CH_3Si)_2C_6H_4$	5	56—57	116—117/1	—	—	—	—	—	46,71	—	—	—	46,24 45,58
p-ClC_6H_4Cl + + C_6H_6	CH_3SiHCl_2**	CH_3SiCl_3	22	$C_6H_5SiCl_2CH_3$	15	—	—	—	—	—	—	—	—	—	—	—	—
				p-$ClC_6H_4SiCl_2CH_3$	19	—	80—83/2	1,5348	1,2861	—	—	—	—	—	—	—	—
				p-$(CH_3Cl_2Si)_2C_6H_4$	8	56—57	116—118/1	—	—	—	—	—	—	—	—	—	—

* p-ClC_6H_4Cl : R_nSiHCl_{3-n} : C_6H_6 = 1 : 1 : 1

** p-ClC_6H_4Cl : R_nSiHCl_{3-n} : C_6H_6 = 1 : 2 : 2.

When β-chloronaphthalene was used in the reaction, as with α-chloronaphthalene, the maximum yields of naphthylchlorosilanes were attained at 640° (τ = 30 sec, β-$C_{10}H_7Cl$: R_nSiHCl_{3-n} = 2:1). The yield of β-naphthyltrichlorosilane was 51% and that of β-naphthylmethyldichlorosilane was 41%.

The naphthylchlorosilanes obtained were methylated with the aid of CH_3MgBr. α-$C_{10}H_7Si(CH_3)_3$, which was obtained in 80% yield, had b. p. 118-119°/3 mm; n_D^{20} 1.5882; d_4^{20} 0.9880.

Found %: C 78.10; 78.13; H 8.00; 7.88; Si 13.92; 13.75.

β-$C_{10}H_7Si(CH_3)_3$, which was obtained in 78% yield, had b. p. 102-103/1 mm; n_D^{20} 1.5725; d_4^{20} 0.9698.

Found %: C 78.17; 78.05; H 8.38; 8.30; Si 13.80; 13.96. $C_{13}H_{16}Si$. Calculated %: C 77.92; H 8.04; Si 14.04.

The infrared absorption spectra of the naphthyltrimethylsilanes were plotted. It was found that when α-chloronaphthalene was used, only α-naphthylchlorosilanes were formed; when β-chloronaphthalenes was used, only β-naphthylchlorosilanes were formed. Thus, no isomerization of chloronaphthalenes was observed under the reaction conditions and their reaction with silicon hydrides proceeded only through the C −Cl bond.

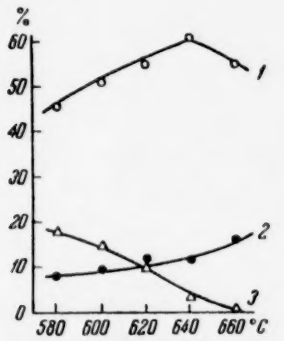

Fig. 1. Relation of the yields of α-$C_{10}H_7SiCl_3$ (1) and $SiCl_4$ (2) and the degree of conversion of $HSiCl_3$ (3) to the temperature in the reaction zone α-$C_{10}H_7Cl$: $HSiCl_3$ = 2:1.

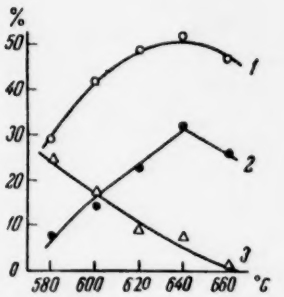

Fig. 2. Relation of the yields of α-$C_{10}H_7SiCl_2CH_3$ (1) and CH_3SiCl_3 (2) and the degree of conversion of CH_3SiHCl_2 (3) to the temperature in the reaction zone α-$C_{10}H_7Cl$:CH_3SiHCl_2 = 2:1.

The reaction of silicon hydrides with p-dichlorobenzene was also accomplished at 640° and a contact time of the reagents of 30 sec. As p-dichlorobenzene has m. p. 53°, the reagents were introduced into the reaction zone in benzene solution in the following proportions: p-ClC_6H_4Cl : R_nSiHCl_{3-n} : C_6H_6 = 1:1:1 and 1:2:2. In the case of the first proportion, for the pair of reagents p-ClC_6H_4Cl and $HSiCl_3$, the yield of p-chlorophenyltrichlorosilane was 29% and that of p-bis-(trichlorosilyl)-benzene, 4%, while in the case of the second proportion, these values were 30 and 15%, respectively, and in this case 12% of phenyltrichlorosilane was formed.

For the pair of reagents p-ClC_6H_4Cl and CH_3SiHCl_2, the yield of p-chlorophenylmethyldichlorosilane was 20% and that of p-bis-(methyldichlorosilyl)-benzene was 5% (first proportion), while these values were 19 and 8.5%, respectively (second proportion); in addition, 15% of phenylmethyldichlorosilane was obtained in the second case. Bis-(chlorosilyl)-benzene, obtained both from $HSiCl_3$ and CH_3SiHCl_2, was methylated with the aid of CH_3MgBr and the samples of bis-(trimethylsilyl)-benzene obtained were identical.

p-$(CH_3)_3SiC_6H_4Si(CH_3)_3$, which was obtained in 80% yield, had b. p. 116°/1 mm and m. p. 92-93°; a mixture with authentic p-bis-(trimethylsilyl)-benzene melted at 92°.

Found %: C 65.52; 65.40; H 10.07; 10.00; Si 24.68; 24.80. $C_{12}H_{22}Si_2$. Calculated %: C 65.05; H 9.91; Si 25.04.

The infrared spectrum of the bis-(trimethylsilyl)-benzene synthesized confirmed that the structure was that of a p-disubstituted benzene. Thus, no isomerization of p-dichlorobenzene was observed under the reaction conditions and the reaction of the compound with silicon hydrides proceeded only at the C—Cl bond.

The experimental results are given in Table 1 (reaction zone temperature 640°, contact time 30 sec, ratio of $ArCl : R_nSiHCl_{3-n} = 2:1$).

Interesting results were obtained on investigating the high-temperature condensation of ethyldichlorosilane with various aryl chlorides.

At a temperature above 550°, ethyldichlorosilane undergoes pyrolytic decomposition with the formation of ethylene and ethane. Silyl radicals are probably formed as intermediate particles and these react with an aryl chloride. Together with the direct formation of silyl radicals, there is the possibility of the formation of an Si—H bond instead of an Si—C bond. This is supported by the analysis of the reaction products. Thus, in the reaction of chlorobenzene and ethyldichlorosilane (ratio of 2:1), at 560° (τ = 40 sec) and 700° (τ = 30 sec), the reaction products were found to contain the alkyl- and arylchlorosilanes given in Table 2.

TABLE 2

At 560°	Yield %	At 700°	Yield %	At 560°	Yield %	At 700°	Yield %
$C_2H_5SiHCl_2$	27	$HSiCl_3$	5	$C_6H_5SiCl_3$	12	$C_6H_5SiCl_3$	23
$C_2H_5SiCl_3$	21	$SiCl_4$	9	$C_6H_5SiC_2H_5Cl_2$	8	$C_6H_5SiC_2H_5Cl_2$	3
$C_6H_5SiHCl_2$	9	$C_2H_5SiCl_3$	15	$(C_6H_5)_2SiCl_2$	3	$(C_6H_5)_2SiCl_2$	7

The gaseous reaction products were found to contain a considerable amount of ethylene. More extensive pyrolysis occurred at the higher temperature and the phenyldichlorosilane, by reacting with chlorobenzene, was converted completely into phenyltrichlorosilane and diphenyldichlorosilane. Even at a reaction zone temperature of 600°, phenyldichlorosilane could not be detected in the reaction products.

It was possible to carry out the reaction of chlorobenzene not only with ethyldichlorosilane, but also ethyltrichlorosilane and diethyldichlorosilane. In the reaction of $C_2H_5SiCl_3$ with C_6H_5Cl (ratio of 1:1 at 620° with τ = 30 sec), only 20% of the starting ethyltrichlorosilane was recovered. Phenyltrichlorosilane was isolated in 29% yield. Analysis of the gaseous reaction products showed that they contained (in vol. %): ethylene 71, ethane 14.2, hydrogen 7.3, and methane 4.2. In the reaction of chlorobenzene with diethyldichlorosilane (ratio of 1:1 at 550° with τ 30 sec), the reaction products were found to contain 5% of phenyldichlorosilane, 6% of phenylethyldichlorosilane, and 5% of diphenyldichlorosilane.

The reaction of ethyldichlorosilane with α-chloronaphthalene was carried out at 560° with a contact time of 30 sec (α-$C_{10}H_7Cl : C_2H_5SiHCl_2$ = 2:1). While the reaction with chlorobenzene under similar conditions gave only 8% of phenylethyldichlorosilane, the yield of α-naphthylethyldichlorosilane reached 21% (b. p. 176-177/5; n_D^{20} 1.5995; d_4^{20} 1.2224). In addition, about 30% of α-naphthyltrichlorosilane was formed.

The procedures described previously [2] were used in the present work for carrying out the experiments and analyzing the mixtures of substances obtained.

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COMPOSITION OF THE PRODUCTS AND KINETICS OF ETHYLENE OXIDE-INITIATED BUTANE CRACKING

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It was observed long ago that propane, butane, isobutane, and pentane [1, 2] undergo decomposition at 400° when introduced into a zone where ethylene oxide is decomposing, though they are not decomposed on their own. In some investigations it has been shown that decomposing ethylene oxide has a catalytic action on the thermal decomposition of ethylene, ethyl ether, acetaldehyde, and other compounds [3]. On the other hand, a study of the pyrolysis of ethylene oxide has shown that the decomposition involves radicals [4, 5]. These facts provided grounds for considering a radical-chain mechanism for the effect of ethylene oxide on the thermal decomposition of organic molecules [4]. Although much work [6-11] has been devoted to the mechanism of ethylene oxide decomposition, this problem cannot be considered solved. Nonetheless, as a result of the investigation of A. I. Terenin on the triplet excited state of molecules [12], it can probably be assumed that at least the photochemical decomposition and apparently the thermal decomposition of the oxide proceeds by a radical mechanism [8].

In the present work we studied the initiating action of ethylene oxide on butane cracking. Only single experiments in this direction have been reported [2]. The composition of the products and the kinetics of butane cracking, initiated by ethylene oxide, were studied by a static method in a high-vacuum apparatus, consisting of three successively connected sections: a kinetic apparatus for studying the cracking of butanes in relation to a change in pressure, an apparatus for separating the cracking products by chromathermography, and an apparatus for the combustion of hydrogen and methane and the determination of CO [14].

TABLE 1

Composition of Products from Initiated Cracking of Butanes (450°, P_{mix} = 200 mm, t = 10 min)

	Butane				Isobutane	Ethylene oxide
	ethylene oxide added (vol. %)					450°, 40 mm
	1	3	5	10	10	
CO	0,25	0,47	0,82	1,75	1,5	50,84
H_2	0	0,61	0,62	0,88	6,02	11,86
CH_4	1,52	5,0	6,8	7,3	4,51	27,12
C_2H_4	1,73	2,72	3,26	4,4	0,9	1,52
C_2H_6	1,47	3,0	3,5	4,61	1,1	7,28
C_3H_6	1,37	5,0	6,6	7,6	4,02	—
C_3H_8	0,36	0,43	0,45	0,76	1,75	1,36
C_4H_8	0	0,57	0,62	0,76	5,89	—
C_4H_{10}	93,4	82,2	77,3	71,9	74,29	—
Percent decomposition	6,5	17,8	22,7	28,1	25,7	
Chain length	12,4	17,6	12,6	7,3	7,2	

The results of studying the composition of the products (t = 10 min) and the kinetics of initiated butane cracking at 450°C with an initial pressure of the hydrocarbon–oxide mixture equal to 200 mm Hg over the ethylene oxide concentration range of 1-10% are given in Table 1 and Figs. 1-3.

The data presented in Table 1 on the composition of the products show that the addition of small amounts of ethylene oxide produced considerable cracking of butanes, which hardly occurred at 450° in the absence of oxide. In this case the products of initiated cracking of butanes contained all the characteristic products of the thermal cracking of butanes at higher temperatures (550-600°). Small amounts of oxide (1-3%) were most effective. The increase in the percent decomposition became progressively less with successive increases in the additive concentration. Thus, with an increase in the oxide concentration from 1 to 3%, the percent decomposition increased from 6.5 to 17.8%, i.e., almost in proportion to the additive concentration, but with a further increase in the amount of additive from 5 to 10%, the percent decomposition increased only from 22.7 to 28.1%. Consequently, saturation is approached in the initiating action and one may expect an

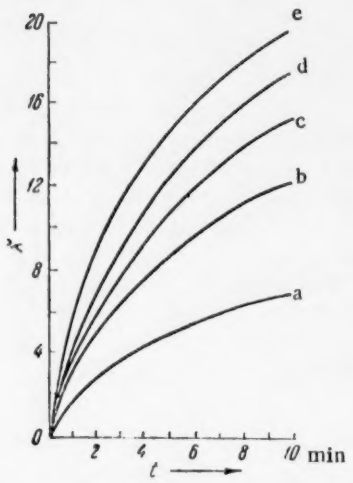


Fig. 1. Effect of added ethylene oxide on the extent of butane decomposition. C_2H_4O concentration: a) 1%; b) 3%; c) 5%; d) iso-C_4H_{10} + 10%; e) n-C_4H_{10} + 10%.

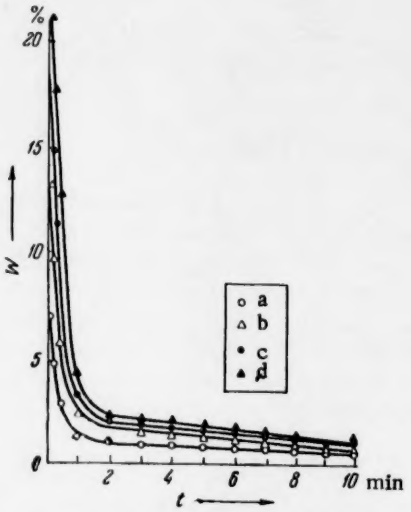


Fig. 2. Effect of added ethylene oxide on the rate of initiation of butane cracking: a) 1% added; b) 3%; c) 5%; d) 10%.

initiation limit, as was predicted by one of us [13] and clearly demonstrated experimentally by us for the cracking of butanes initiated by added azomethane.

When 10% of oxide was added, the decomposition reached approximately 30% (under otherwise equal conditions, the extent of the initiated cracking of isobutane was less than that of butane). The decomposition of ethylene oxide itself cannot explain the extensive decomposition of the butanes nor the over-all composition of the products as the decomposition of ethylene oxide in a pure state gives small amounts of H_2, CH_4, C_2H_4, C_2H_6, and C_3H_8 (see Table 1).

In the initiated cracking of butane, the ratios of the yields of pairs of products ($CH_4-C_3H_6$, $C_2H_6-C_2H_4$, and $H_2-C_4H_8$) had the normal values for thermal cracking at higher temperatures, but with a low initiator concentration (1%) there were similar amounts of demethanization and deethanization, in contrast to normal cracking. With an increase in the ethylene oxide concentration (3-5%) demethanization began to predominate, as occurs in normal cracking. This curious fact indicates that under the action of the initiator there is a shift in the direction of demethanization in the cracking, as has been observed in the normal cracking of butanes. The observed shift can be explained most probably with the aid of the hypothesis on the isomerization of butyl radicals to secondary butyl radicals [14].

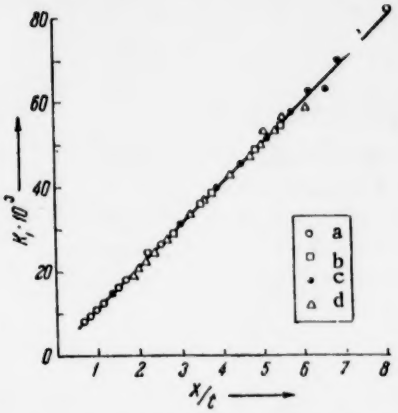


Fig. 3. Effect of the extent of initiated cracking of butane on the monomolecular rate constant: a) 1% of additive; b) 3%; c) 5%; d) 10%.

The high yield of CH_4, C_2H_6, and H_2 in comparison with normal cracking is explained by decomposition of the oxide. The mean chain length, determined from the ratio of total olefins to carbon monoxide, first increased with an increase in the amount of additive, passed through a maximum, and then again fell to a limit, which was also observed in normal cracking.

A similar picture was observed in the initiated cracking of isobutane with retention of the predomination of the decomposition directions which are characteristic of normal cracking [14]. The somewhat high yield of H_2, CH_4, and C_2H_6 was connected with decomposition of the oxide.

The results of studying the kinetics of initiated cracking of butanes with respect to the change in pressure in the reaction zone, allowing for decomposition of the oxide, are given in Figs. 1-3.

Curves showing the relation of the extent of butane decomposition (X) to time (Fig. 1) show that the initiation effect depends on the ethylene oxide concentration and are close approximations to the relation expressing saturation in the initiating action:

$$X = b(1 - e^{-aT_0}), \qquad (1)$$

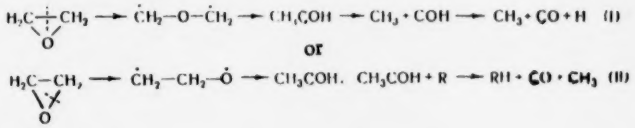
in which a and b are some constants, T_0 is the oxide concentration, and X is the extent of decomposition (expressed in mm Hg).

The initial rate of initiated cracking of butane ($W = \frac{\Delta P}{P \Delta t} \cdot 100$) increased with an increase in the initiator concentration and in each individual case, fell rapidly with time to reach a certain limiting value, which was practically independent of the initial concentration of additive (Fig. 2). Curves for the rate of initiated cracking were analogous to the curve for self-inhibiting or retarded normal cracking, which we obtained previously [15].

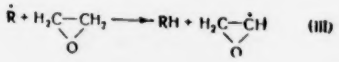
The kinetics of initiated cracking, like normal cracking, have the character of a process which is inhibited by its own products and are described by the equation of Dintsess and Frost for a self-inhibiting reaction [16]: $\frac{1}{t} \ln \frac{1}{1-X} = k_0 + \beta \frac{X}{t}$ (Fig. 3).

The mechanism and kinetics of ethylene oxide-initiated cracking of butanes may be interpreted by means of the theory of the double action of additives that one of us proposed [13, 14, 17] in which not just the initiating, but also the inhibiting properties of ethylene oxide are considered.

The initiating properties of ethylene oxide apparently arise from decomposition reactions involving biradicals:

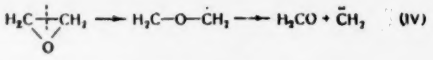

H_2C-CH_2 (O) $\rightarrow \dot{C}H_2-O-\dot{C}H_2 \rightarrow CH_3\dot{C}OH \rightarrow CH_3 \cdot COH \rightarrow CH_3 \cdot CO + H$ (I)
or
H_2C-CH_2 (O) $\rightarrow \dot{C}H_2-CH_2-\dot{O} \rightarrow CH_3COH$. $CH_3COH + R \rightarrow RH + CO \cdot CH_3$ (II)

The retarding properties may be connected with the reaction



in which the radical with the ring structure is less active and tends to dimerize or polymerize.

However, if the role of R in reaction (III) is played by a methylene radical, arising, for example, from the reaction



(IV)

by reacting with ethylene oxide it may give a CH_3 radical which is capable of developing a chain.

On the basis of the experimental data of the kinetics of decomposition and the corresponding radical–chain scheme of initiated cracking, in which we neglected the retarding action of the oxide and the products on the decomposition, we calculated the rate constant of ethylene oxide decomposition (450°, $K_0 = 0.20\ min^{-1}$) and the activation energy of the decomposition, that was found to equal 51.2 kcal/mole, which is in good agreement with the values of 52 and 50 kcal, found in previous work on decomposition of the oxide [1, 7].

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MECHANISM OF THE CYCLIZATION OF PSEUDOIONONE

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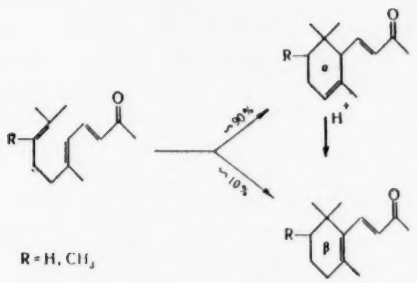
During the study of structural direction of the cyclization of pseudoionone, we showed [1] that the primary product of this reaction is α-ionone, which, depending on the cyclization conditions (temperature, reaction time, and amount of cyclizing agent) is capable of isomerizing to β-ionone to some extent. A more detailed examination of the data we obtained showed that the formation of β-ionone under the conditions used could not be ascribed solely to isomerization of α-ionone as the amount of β-isomer in the mixture of ionones formed was always greater than in the direct isomerization of pure α-ionone under the same conditions and this discrepancy was beyond the limits of experimental error. In addition, it was shown that even under conditions under which there was practically no isomerization of α-ionone to β-ionone (−70°), 10-12% of the β-isomer was still formed.



R = H, CH_3

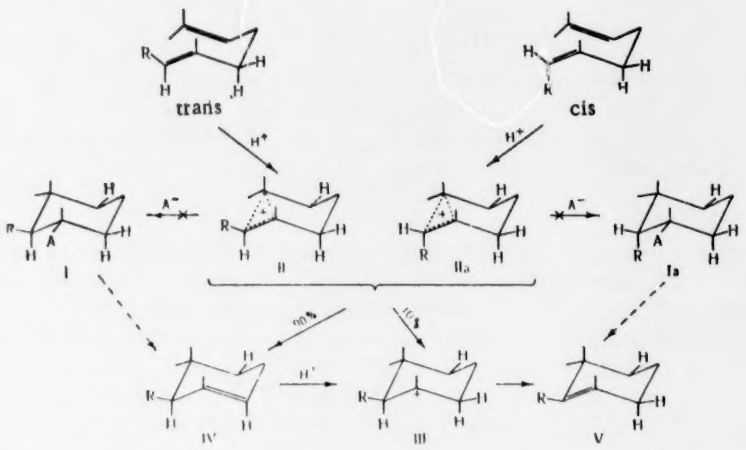
It was found that the same rule was observed in the cyclization of pseudoirone at −70°. In this case also, mainly α-isomer with a little (about 7%) of β-irone was formed. Like β-ionone, β-irone may be obtained in a pure form by isomerization of the α-isomer.

The cyclization conditions we used for pseudoionone and pseudoirone were the conditions for stereospecific cyclization [2] and it was important to determine the extent to which the structural direction of this reaction depends on the geometrical isomerism of the starting ketone. If there were a similar relation, it might be considered that the formation of a small amount of β-isomer was the result of cyclization of the cis form, which could be present in the starting pseudoionone and pseudoirone. According to the data of Schinz [3], the cyclization of cis- and trans-pseudoionones leads to the same mixture of ionones, but the cyclization conditions he used compel one to treat this conclusion with care.

For a conclusive and unequivocal solution of this problem, which is extremely important for determining the mechanism of the cyclization, we studied the cyclization of pure trans-pseudoionone, a mixture of cis and trans isomers obtained from natural citral and containing 12% of cis-pseudoionone [3], and a synthetic mixture of cis and trans isomers (1 : 1) under stereospecific cyclization conditions such that the possibility of isomerization of α-ionone to β-ionone was practically excluded. It was found that in all these cases we obtained

completely identical mixtures of cyclization products, containing (according to ultraviolet spectral data) 85-90% of α-ionone and 10-12% of the β-isomer. These data unequivocally demonstrate that the structural direction of pseudoionone cyclization is independent of the cis or trans configuration at the 6,7-double bond of the starting ketone and the formation of the given amount of β-ionone is the result of an independent parallel reaction.

Starting from the ideas of Ružicka [4] on the role of a nonclassical cation in cyclizations of isoprenoids, we may represent the mechanism of pseudoionone cyclization in the following way, which corresponds most completely to all the rules established above.



Since it was found that the structural direction of the cyclization is independent of the configuration of the starting ketones, the formation of the final reaction products does not proceed through the intermediate, sterically fixed forms (I and Ia), the stabilization of which in accordance with the general rules of elimination reactions [5] should give α-ionone from trans-pseudoionone and β-ionone from the cis isomer. On this basis, it is necessary to assume that the main direction of the stabilization of both possible nonclassical cations (II and IIa), corresponding to the trans and cis forms of pseudoionone, is direct ring closure with migration of the double bond to the α-position in analogy with the Prince reaction and cationotropic rearrangements. Such a reaction direction explains the initial and predominant formation of α-ionone (IV) and the independence of this result of the cis and trans configuration of the starting ketone.

However, together with this main reaction there is also recombination of the nonclassical cations (II and IIa) to the same classical cation (III) and the most probable stabilization of this occurs as a result of elimination of the tertiary hydrogen atom with the formation of the conjugated system of the β-isomer (V). This side reaction of the cyclization explains the appearance in the mixture of the β-ionone, the amount of which must depend solely on the ratio of the rate of formation of cation (III) and the rate of direct cyclization of the nonclassical cations to α-ionone (IV).

It was not possible to study the kinetics of this side, parallel reaction as the isomerization of α-ionone to β-ionone must also proceed through the intermediate formation of the classical cation (III). The only possibility if influencing the rate of recombination of the π-complex to the classical cation might be a change in the nature of the solvent in which the low-temperature acid cyclization of pseudoionone must be performed. However, an attempt to replace nitroparaffins by other solvents (hydrocarbons, alkyl halides, liquid SO_2, ethers, esters, aliphatic acids, etc.) was unsuccessful because at low temperature these solvents either dissolve sulfuric acid with difficulty or almost completely suppress its acid properties.

The voluminous material on the cyclization of isoprenoid compounds [6] shows that the exclusive or predominant formation of α-isomers is the general rule in this reaction and therefore the cyclization mechanism proposed is apparently general. Cyclization mechanisms discussed previously on the example of pseudoionone [7, 8] cannot be considered satisfactory as they do not reflect this basic rule.

EXPERIMENTAL *

In the cyclization reaction we used: 1) pseudoionone obtained from natural citral; 2) trans-pseudoionone obtained from pure geraniol (regenerated from the crystalline diphenylurethan with m. p. 80° and freed from traces of diphenylamine by chromatography on alumina) by oxidation and simultaneous condensation with acetone [3]; the trans-pseudionone used had b. p. 112-114° at 1 mm, n_D^{20} 1.5308, and gave 90 per cent yield of a 2,4-dinitrophenylhydrazone with m. p. 148-149° (methanol–dioxane) [3]; 3) a mixture of trans- and cis-pseudoionones obtained in the following way. Purified geraniol was isomerized to nerol** in the presence of sodium hydroxide [10]. The unreacted geraniol was separated by two treatments with calcium chloride. The residue which did not react with calcium chloride was converted into the diphenylurethan, when a further small amount of geraniol diphenylurethan was isolated from the mother solution of the diphenyl urethan. The uncrystallizable residue after hydrolysis was converted into the alcohol, which, after chromatography on alumina gave a diphenylurethan with m. p. 54-60° [11]. The oxidation of this alcohol with simultaneous condensation with acetone yielded a mixture of trans- and cis-pseudoionones, whose composition was assessed by fractional crystallization of their 2,4-dinitrophenylhydrazones (methanol–dioxane). By this method it was shown that the mixture contained equal amounts of trans- and cis-pseudoionones, the 2,4-dinitrophenylhydrazones of which melted at 148-149° (methanol–dioxane) and 118-120° (methanol), respectively [3].

Cyclization of pseudoionones. a. To a solution of 3 ml of 100% sulfuric acid in 10 ml of nitropropane at −70° was added a cooled mixture of 2.0 g trans-pseudoionone and 5 ml of nitropropane over a period of 4 min. After the reaction mixture had been stirred for 1 hr, it was decomposed by being poured (with stirring) into a mixture of 40 ml of water with ice and 30 ml of hexane. The aqueous portion was extracted three times with hexane and the hexane solution washed with water, sodium bicarbonate solution, and again with water and dried over potassium carbonate. After removal of the hexane and nitropropane, the residue was vacuum distilled. We obtained 1.55 g of a substance with b. p. 75-78°/1 mm and n_D^{20} 1.500; the residue was 0.3 g. The ultraviolet spectrum of this cyclization product had λ_{max} 227 mμ, ε 13400, which corresponds to a 90% content of α-ionone and 12% of β-ionone.

b. The cyclization of a mixture of trans- and cis-pseudoionones (1:1) was carried out under strictly analogous conditions and this yielded 0.8 g of a product with b. p. 81-84°/1 mm and n_D^{19} 1.4990; the residue was 0.5 g. The ultraviolet spectrum of the cyclization product had λ_{max} 227 mμ, ε 12080 and λ_{max} 294 mμ, ε 1275, which corresponds to 83% of α-ionone and 11% of β-ionone.

c. Cyclization of pseudoionone from natural citral under the same conditions yielded 1.5 g of a product with b. p. 78-81°/1 mm and n_D^{19} 1.5000; the residue was 0.3 g. The ultraviolet spectrum had λ_{max} 227 mμ, ε 12790 and λ_{max} 294 mμ, ε 1306, which corresponds to 86% of α-ionone and 12% of β-ionone.

d. An attempt to isomerize α-ionone to β-ionone under strictly analogous conditions to those described above led to the isolation of practically unchanged α-ionone. Under these conditions isomerization proceeded extremely slowly and after 10 hr the β-ionone content increased from 5% in the original α-ionone to 8% in the reaction product. The ultraviolet spectrum of the original α-ionone had λ_{max} 227 mμ, ε 13300 and λ_{max} 297 mμ, ε 564, which corresponds to 93% of α-ionone and 5% of β-ionone; after the reaction the ionone obtained showed λ_{max} 227 mμ, ε 12600 and λ_{max} 297 mμ, ε 830, i.e., it contained 87% of α-ionone and 8% of β-ionone.

Cyclization of pseudoirone. The 3-methyllinalool needed for the synthesis of pseudoirone was obtained by the addition of hydrogen bromide to 2,3-dimethylbutadiene, condensation of the bromide with sodioacetoacetic ester, subsequent acetylene synthesis, selective hydrogenation and conversion into the primary alcohol in analogy with the synthesis of linalool [9]. Oxidation of 3-methyl linalool with simultaneous condensation with acetone yielded pseudoirone with b. p. 105-116/1 mm and $n_D^{18.5}$ 1.5340.

To a solution of 15 ml of 100% sulfuric acid in 50 ml of nitropropane at −70° was added a cooled solution of 10 g of pseudoirone in 25 ml of nitropropane over a period of 20 min. After it had been stirred for 1 hr, the reaction mixture was decomposed by pouring (with stirring) into a mixture of 200 ml of water and ice and 150 ml of hexane. The aqueous portion was extracted three times with hexane and the hexane solution washed with water, sodium bicarbonate solution, and again with water and dried over potassium carbonate. After removal of the

*Carried out with the assistance of T. N. Chernova.

**Literature data [9] on the possibility of isolating nerol by chromatography of the reaction product of geranyl bromide and potassium acetate in dimethylformamide solution on alumina was found to be incorrect.

hexane and nitropropane, the residue was vacuum distilled. We obtained 7.3 g of cyclization product with b. p. 99-103°/1 mm and n_D^{20} 1.5020. Its ultraviolet spectrum had λ_{max} 226.5 mμ, ε 13610 and λ_{max} 294 mμ, ε 912, which corresponds to 85% of α-irone and 7% of β-irone.

The addition of one equivalent of hydrogen to the cyclization product did not lead to a compound giving an individual semicarbazone so that it must be considered that the irone obtained was evidently a mixture of stereoisomeric α-irones [12]. Special tests of the irone showed that low-temperature cyclization of pseudoirone led to a product with very valuable perfume properties.

Isomerization of α-irone to β-irone. To a solution of 3.0 ml of 100% sulfuric acid in 10 ml of nitromethane at −20° was added a mixture of 2.0 g of the α-irone obtained in 5 ml of nitromethane over a period of 3 min. Over the following 3 min, the temperature of the mixture was raised to +10° and the reaction mixture was stirred for a further 10 min. The decomposition and isolation were carried out by the usual method. We obtained 1.75 g of isomerization product with b. p. 90-94°/1 mm and n_D^{18} 1.5140. From 0.8 g of the product we obtained 0.4 g of β-irone semicarbazone with m. p. 167-168° (from alcohol) [12].

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COMPARATIVE HYDROGENATION OF SODIUM PROPIOLATE ON Pt, Pd, and Ni CATALYSTS

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In the present article we present experimental data obtained during a study of the catalytic properties of nickel, platinum, and palladium in the hydrogenation of sodium propiolate. The hydrogenation proceeds according to the scheme:

$$\underset{\text{Sodium propiolate}}{CH \equiv C - COONa} + H_2 \rightarrow \underset{\text{Sodium acrylate}}{CH_2 = CH - COONa} + H_2 \rightarrow \underset{\text{Sodium propionate}}{CH_3 - CH_2 - COONa}$$

The Raney nickel was prepared by leaching a Ni–Al alloy (30% Ni). The platinum was obtained from the oxide [1] and the palladium from palladium hydroxide on barium sulfate [2] by reduction with hydrogen directly in the hydrogenation flask. A 0.1 N aqueous solutuon of NaOH was used as the solvent. Before hydrogenation, the catalyst in the solvent was saturated with hydrogen up to the reversible hydrogen potential. During the hydrogenation, the potential of the catalyst was measured by the compensation method relative to a 0.1 N calomel electrode. Either 0.1, 0.2, or 0.3 g of propiolic acid was introduced into the hydrogenation flask and converted to the salt by netralization with sodium hydroxide. Experiments were carried out at 60, 40, 20, and 5°. Four successive experiments at different temperatures were carried out on the same sample of platinum and palladium.

Figure 1 shows kinetic and potential curves for the hydrogenation of 0.262 g of sodium propiolate on Pd, Ni, and Pt at 40° in aqueous alkali (0.1 N NaOH).

It seemed to us that the kinetic curves could be divided into two sections: from the beginning of hydrogenation to the absorption of 64 ml of hydrogen and from this point to the end. Polarographic data showed that in the stage corresponding to the first section of the curve the triple bond of sodium propiolate was 93-94% hydrogenated and in the second stage, the double bond of sodium acrylate and the remaining triple bonds of sodium propiolate were hydrogenated.

As Fig. 1 shows, the triple bond was hydrogenated with a monotonically falling rate on Raney nickel. The transition from hydrogenation of the triple bond to the double bond was expressed by a sharp break on the kinetic curve, after which there was an increase in the reaction rate, characteristic of hydrogenation of a double bond.

Thus, the rate of hydrogenation of the triple bond of sodium propiolate was less than the rate of hydrogenation of the double bond of sodium acrylate. The displacement of the catalyst potential in an anodic direction when the salt was introduced into the solution was 60 mv, but its change during hydrogenation of the triple bond was very slight. The change from hydrogenation of the triple to the double bond on palladium was less clearly expressed. The rate of hydrogenation of the triple bond was lower than that of the double bond but gradually increased. The catalyst potential was displaced 90 mv into the anode region and remained constant until most of the triple bonds had been hydrogenated.

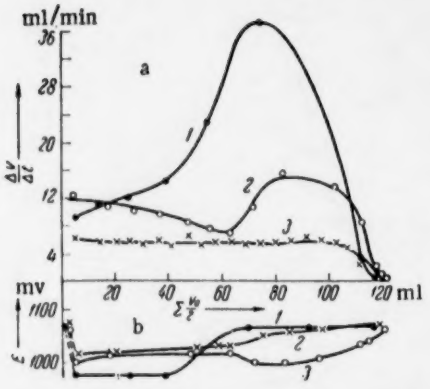

Fig. 1. Kinetic (a) and potential (b) curves of the hydrogenation of 0.262 g of sodium propiolate. Solvent 0.1 N NaOH in water and t = 40°. 1) On Pd; 2) on Ni; 3) on Pt.

In contrast to the reactions with palladium and Raney nickel, the hydrogenation of sodium propiolate on platinum was almost a zero order reaction, but with quite good selectivity (up to 94%). The displacement of the catalyst potential into the anode region was 50 mv and the triple bond was hydrogenated at a potential of 1020 mv.

The change from hydrogenation of the triple to the double bond was also clearly marked on the potential curves by a sharp change in the catalyst potential. As was noted above, in the hydrogenation of the triple bond of sodium propiolate the catalyst potential remained almost constant. However, toward the end of hydrogenation of the triple bond on Pt and Pd the catalyst potential changed sharply in a cathodic direction with an increase in the absolute value of the potential by 25 mv on Pt and by 85 mv on Pd. However, in the case of Raney nickel the end of hydrogenation of the triple bond was marked by a displacement of the cathode potential in an anodic direction by 20-30 mv.

Thus, while the double bond was hydrogenated at more negative potentials than the triple bond on Pd and Pt, the hydrogenation potential of the double bond was more positive than that of the triple bond on Raney nickel.

The former is completely explainable if it is assumed that molecules with a triple bond are adsorbed more strongly than molecules with a double bond. The somewhat unusual behavior of the catalyst potential during the hydrogenation of the double bond on skeletal Ni is evidently connected with intradiffusion factors and the unequal capacities of the different molecules to penetrate into the pores of the catalyst [3].

In the work we also studied the effect of the sodium propiolate concentration on the kinetics of its hydrogenation. This relation is shown in Fig. 2. This figure shows that the rate of hydrogenation of the triple bond decreased with an increase in the sodium propiolate concentration, while the rate of hydrogenation of the double bond increased. Analogous results were obtained for platinum and palladium.

On the basis of opinions expressed previously [4, 5], we assume that the hydrogenation of the triple bond is limited by the activation of hydrogen. This is evidently connected with the fact that sodium propiolate is firmly adsorbed by the triple bond on the catalyst surface. Naturally, an increase in the sodium propiolate concentration in the solution leads to a lack of active hydrogen on the catalyst surface, which has a negative effect on the rate of hydrogenation of the triple bond that appears to a greater extent on Raney nickel than on palladium. The lack of hydrogen on palladium may be compensated for by the emergence at the catalyst surface of dissolved or subsurface hydrogen, which is used mainly in the hydrogenation of the triple bond.

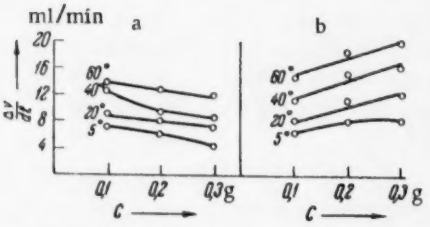

Fig. 2. Effect of sodium propiolate concentration on the rate of its hydrogenation on Raney nickel. The solvent was 0.1 N NaOH in water. a) Rate of hydrogenation of triple bond; b) rate of hydrogenation of double bond.

The double bond of sodium acrylate does not have the capacity to displace hydrogen from the catalyst surface to the same extent as the triple bond. Therefore, in the second half of the reaction the hydrogen can be activated on the catalyst surface and this leads to a considerable increase in the hydrogenation rate on Raney nickel and palladium.

The activation of the unsaturated compound becomes the stage limiting the process. This is indicated by the decrease in activation energy on Raney nickel from 8.0 to 6.0 kcal/mole and on palladium from 10.0 to 7.0 kcal/mole.

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DILATOMETRIC AND SPECTROPHOTOMETRIC INVESTIGATION OF THE FORMATION MECHANISM OF HIGH-MOLECULAR COMPOUNDS OF TUNGSTEN

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The mechanism of the formation of aqueous high-molecular compounds of tungsten, which arise in an acidified solution of normal sodium tungstate, has not been studied sufficiently. One of us [1, 2] established that the reactions occurring here are slow and an important role in them is played by the simultaneous presence in solution of hydronium ions, tungstate ions, and tungstic acid molecules, which react together through the formation of hydrogen bonds. In the crystallization of the compounds from aqueous solution, some of the hydrogen bonds may be replaced by the bond of WO_4^{2-} tetrahedra due to shared oxygen atoms.

We used dilatometry and spectrophotometry to study the kinetics of the processes which occur when normal sodium tungstate is acidified and which lead to the formation of an aquopolytungstate (the paratungstate) and its crystallization from aqueous solution. The dilatometer consisted of a bulb with a capacity of 108 cc and a long capillary. The temperature of the dilatometer was kept constant in a thermostat with an accuracy of ±0.01-0.02°. The volume of solution in the capillary was determined with the ocular of a microscope with an accuracy of $\pm 3 \cdot 10^{-4}$ ml. It was established that the temperature inside the dilatometer equaled the temperature of the thermostat during the whole of the experiment. Solutions of Na_2WO_4, acidified with nitric acid, were sucked through the capillary with the aid of a vacuum apparatus. About 30-40 min elapsed between the acidification and the beginning of the first measurement as this time was necessary for thermal equilibrium to be established. As the process proceeded over several hours, neglecting this time had no effect on the determination of the order of reaction, which was what interested us.

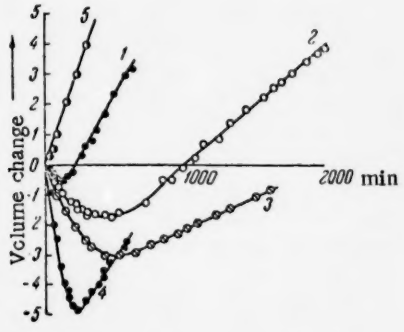

Fig. 1. Dilatometric curves. $Na_2WO_4 \cdot 2H_2O$ concentration 1 mole/liter; one division on the ordinate equals $5.3 \cdot 10^{-3}$ ml. 1) pH 8.2; $H^+/WO_4^{2-} = 0.70$; t = 26.7°; 2) pH 6.3; $H^+/WO_4^{2-} = 1.14$; t = 26.7°; 3) pH 5.7; $H^+/WO_4^{2-} = 1.16$; t = 26.7°; 4) pH 8.2; $H^+/WO_4^{2-} = 0.70$; t = 47.5°; 5) crystallization of pure paratungstate. $Na_{10}W_{12}O_{41} \cdot 28H_2O$ 0.0061 mole/liter.

The curve of the change in volume had a minimum (Fig. 1). The decrease in the solution volume was connected with the formation of the compound, sodium paratungstate, and the increase, with its crystallization. Both branches of the curve were investigated in detail. The order of the formation of the aquopolytungstate with respect to the concentration of WO_4^{2-} ions, calculated from the initial rates, was found to equal 1 (Fig. 2) with a constant ratio of H^+/WO_4^{2-}, where H^+ corresponds to the amount of acid added to the Na_2WO_4 solution.

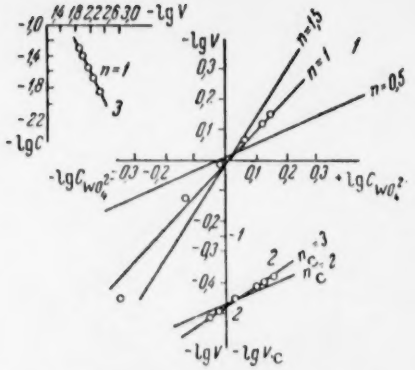

Fig. 2. Determination of the order of formation and of crystallization of sodium paratungstate from dilatometric and spectrophotometric data. 1) Formation of paratungstate (dilatometric method); pH 5.7; H^+/WO_4^{2-} = 1.16; t = 26.7°; 2) crystallization of paratungstate from acidified Na_2WO_4 solution; H^+/WO_4^{2-} = 0.70; pH 8.2; t = 26.7°; 3) formation of hexatungstate ions (spectrophotometric method); H^+/WO_4^{2-} = 0.73; pH 6.6; t = 100°.

We also studied the crystallization of the salt formed. It was established that the increase in solution volume was strictly proportional to the amount of salt crystallized. At pH 8.2 and a Na_2WO_4 concentration of 1 mole/liter, the change in solution volume was $0.6 \cdot 10^{-2}$ ml/g. Since at a given ratio H^+/WO_4^{2-} the amount of sodium paratungstate formed is directly proportional to the Na_2WO_4 concentration, then in the equation for the rate of crystallization of the salt $V_c = K_c C_p^n$, where V is the initial crystallization rate, C_p is the paratungstate concentration, and K_c is a constant, for determining the order of the crystallization process it is possible to replace the paratungstate concentration by the Na_2WO_4 concentration. The order of the crystallization of sodium paratungstate from an acidified solution of normal sodium tungstate with H^+/WO_4^{2-} = const. with respect to the concentration of WO_4^{2-} ions was found to equal 3 (Fig. 2).

The absorption spectra in the ultraviolet region were measured on an SF-4 spectrophotometer with the use of thermostatted quartz cells, 1 cm thick. The absorption spectrum of an acidified Na_2WO_4 solution (Fig. 3), plotted immediately after acidification was a steeply falling curve. However, after a short time on the curve there appeared a plateau with a center at λ_{max} = 256 mμ, characteristic of the spectrum of hexatungstate ions, obtained by decomposition of the paratungstate anion $W_{12}O_{41}^{10-}$ [3]. The kinetics of the formation of hexatungstate ions were studied in detail by measurement of the absorption intensity at λ = 256 mμ with time (Fig. 4). The order of the reaction with respect to WO_4^{2-}, determined from the initial rates with a constant ratio H^+/WO_4^{2-}, was found to equal 1 (Fig. 2). The activation energy was determined from the change in the initial rates V_1 and V_2 in relation to temperature T_1 and T_2 from the formula $V_1/V_2 = e^{-\frac{E}{RT_1}} \Big/ e^{-\frac{E}{RT_2}}$, and was found to equal 10.8 kcal/mole (Fig. 4).

was established that at a paratungstate concentration of ~10^{-5} mole/liter, the decomposition proceeded in two stages (Figs. 3 and 4, curves 7' and 7"):

$$W_{12}O_{41}^{10-} + 28\,H_2O = 2HW_6O_{21}^{5-} + 13.5\,H_2O = 5WO_4^{2-} + 7\,H_2WO_4 + 21\,H_2O.$$

Stage 1 Stage 2

The first stage, which was the dipolymerization of paratungstate ions to hexatungstate ions, was a first order reaction with an activation energy of 6 kcal/mole, while the second stage, corresponding to complete cleavage of hexatungstate ions to WO_4^{2-} and H_2WO_4, had an activation energy of 11.5 kcal/mole and was also first order.

The great difference in the activation energies of the two stages of paratungstate anion decomposition may indicate the presence of different types of chemical bonds in the anion. At higher paratungstate concentrations (~10^3 mole/liter), the process proceeded somewhat differently; the first stage remained the same, while the second stage corresponded not to cleavage of the hexatungstate ion, but to its conversion to an anion related to metatungstate, which was connected with the appearance of a maximum on the spectrophotometric curve (Fig. 3), similar to the maximum of the metatungstate ion [3]. We did not investigate the kinetics of this process in detail.

In the general form, the formation of aqueous high-molecular tungsten compounds may be represented in the following way: When an Na_2WO_4 solution is acidified, a complex is formed in it, which consists of H_2WO_4 molecules, WO_4^{2-} or HWO_4^- ions, and HO_3^+ ions, connected by hydrogen bonds. The molecular weight of such an aggregate may vary, depending on the pH. In more acid solutions it reaches high values due to the addition of further H_2WO_4 molecules [3]. Such complexes are unstable in solution and gradually rearrange with transition

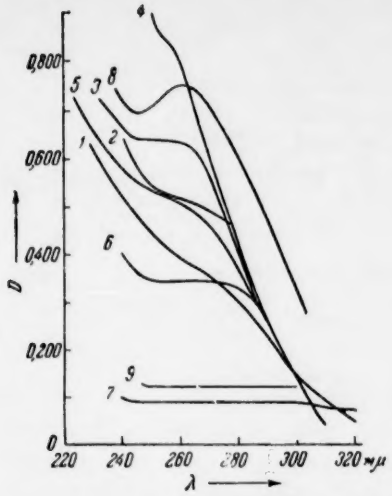

Fig. 3. Ultraviolet absorption spectra. 1) Freshly prepared acidified Na_2WO_4 solution; concentration 0.03 mole/liter; pH 6.6; $H^+/WO_4^{2-} = 0.73$; t = 100°; 2) after 15 min; 3) after 60 min: the solution was diluted 100-fold during the measurements; 4) freshly prepared $Na_{10}W_{12}O_{41}\ 28H_2O$ solution; concentration $2.86 \cdot 10^{-5}$ mole/liter; t = 100°; 5) after 2 min; 6) after 4 hr; 7) after 16 hr; 8) $Na_{10}W_{12}O_{41} \cdot 28\ H_2O$, solution; concentration $2.86 \cdot 10^{-3}$ mole/liter; standing time 10 hr; t = 100°; solution diluted 100-fold during measurements; 9) suspension of H_2WO_4 in water ($\sim 5 \cdot 10^{-3}$ g/liter).

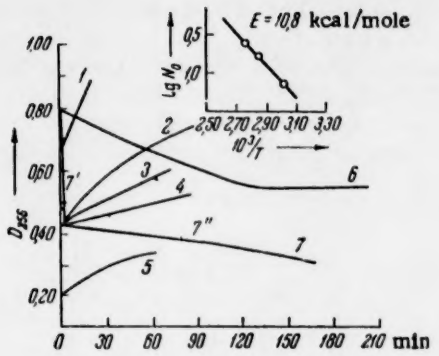

Fig. 4. Change in optical density at λ = 256 mμ, corresponding to the formation of hexatungstate ions in acidified normal tungstate solution and decomposition of paratungstate anion. Formation of hexatungstate ions; pH 6.6; $H^+/WO_4^{2-} = 0.73$. Na_2WO_4 concentration and experiment temperature: 1) 0.05 mole/liter, t = 100°; 2) 0.03 mole/liter, t = 100°; 3) 0.03 mole/liter, t = 79°; 4) 0.03 mole/liter, t = 60°; 5) 0.015 mole/liter, t = 100°. The solutions were diluted 100-fold during the measurements. Decomposition of paratungstate anion. $Na_{10}W_{12}O_{41} \cdot 28H_2O$ concentration $2.8 \cdot 10^{-5}$ mole/liter; 6) t = 43.7°; 7) t = 100° (two decomposition stages, corresponding to curves 7' and 7'', were observed).

of a hydrogen bond into a bond through an oxygen bridge with the elimination of water. There may also be partial decomposition of the complex. In this case, the reaction rate

$$V = KC_{comp}^{n},$$

where C_{comp} is the concentration of complexes and K is the reaction rate constant. When H^+/WO_4^{2-} = const., the value C_{comp} is directly proportional to the Na_2WO_4 concentration:

$$C_{comp} = \alpha C_{WO_4^{2-}} \qquad (2)$$

(α is the proportionality coefficient). By substituting (2) in (1), we obtain $V = K(\alpha C_{WO_4^{2-}})^n$ and then $\lg V = \lg K + n \lg \alpha + n \lg C_{WO_4^{2-}}$. For the rearrangement process, n should equal 1, which corresponds to the experimental data we obtained.

From this point of view, for example, the formation of sodium paratungstate $Na_{10}W_{12}O_{41} \cdot 28H_2O$ may be represented in the following way:

$$7\,H^+ + 6\,WO_4^{2-} \rightarrow H_7W_6O_{24}^{5-}$$

$$H_7W_6O_{24}^{5-} \xrightarrow{-H_2O} H_5W_6O_{23}^{5-} \xrightarrow[\text{fast}]{-H_2O} H_3W_6O_{22}^{5-} \xrightarrow{-H_2O} HW_6O_{21}^{5-}$$

$$2\,HW_6O_{21}^{5-} \xrightarrow[\text{slow}]{} W_{12}O_{41}^{10-} + H_2O \text{ (dimerization)}$$

The rate of the process is limited by the kinetics of rearrangement of the intermediate metastable complex $H_7W_6O_{24}^{5-}$, which is built up solely on the basis of hydrogen bonds and also contains bound water. The structural formula of this complex may be represented either as $[H_3O(WO_4)_3(HWO_4)_3(H_3O)_3(H_2O)_n]^{5-}$ or $[3H_2WO_4(WO_4)_2(HWO_4)nH_2O]^{5-}$. In the intermediate polyanions obtained there are different combinations of hydrogen bonds and bonds through oxygen bridges. At higher Na_2WO_4 concentrations, each of these polyanions are capable of dimerization to give anions whose composition lies within the range $H_{10}W_{12}O_{46}^{10-}$ . . . $W_{12}O_{41}^{10-}$.

According to our ideas, the over-all formulas of paratungstate may be represented as:

1) $Na_{10}H_{10}W_{12}O_{46}\cdot 23H_2O$; 2) $Na_{10}H_8W_{12}O_{45}\cdot 24H_2O$;
3) $Na_{10}H_6W_{12}O_{44}\cdot 25H_2O$; 4) $Na_{10}H_4W_{12}O_{43}\cdot 26H_2O$;
5) $Na_{10}H_2W_{12}O_{42}\cdot 27H_2O$; 6) $Na_{10}W_{12}O_{41}\cdot 28H_2O$.

In the first formula there are ten hydrogen bonds and in the last all the bonds through oxygen bridges. It should be noted that the hydrogen atoms forming the hydrogen bonds cannot be replaced as this would lead to decomposition of the given anion. The correspondance of paratungstate to one of the given formulas depends on the conditions under which it is prepared and exists. Thus it is possible to explain the apparent contradiction that according to x-ray structural data [4], paratungstate corresponds to the anion $W_{12}O_{46}^{10-}$, and not $W_{12}O_{41}^{10-}$, as follows from chemical investigations.

An analogous case was recently described for potassium pentaborate [5], the state of the hydrogens in which, as established by nuclear proton resonance, corresponds to the formula $KH_4B_5O_{10}\cdot 2H_2O$. The previously proposed formula $K(H_3O)_2(H_2B_5O_{10})$ is less probable [6].

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VINYL COMPOUNDS IN DIENE SYNTHESIS:

STEREOSPECIFIC DIRECTION OF DIENE SYNTHESIS OF VINYL ARYL ETHERS WITH CYCLOPENTADIENE IN RELATION TO TEMPERATURE

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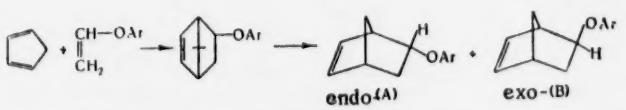
In previous communications it was shown that vinyl and thiovinyl ethers will undergo diene synthesis with cyclopentadiene and hexchlorocyclopentadiene [1-3]. It was found that the double bond in vinyl aryl and thiovinyl ethers has the greatest dienophilic activity. For a more complete characterization of the adducts obtained, it was necessary to study their stereochemistry and also the stereospecific direction of the reaction in relation to temperature.

The investigation of the stereochemistry of the reaction of cyclic dienes with dienophiles containing groups with multiple bonds or unshared pairs of electrons led to Alder's rule [4] on the "accumulation of unsaturation," according to which the adduct with an endo configuration is formed predominantly. The predominant formation of the endo isomer is connected with favorable kinetic factors, though the exo isomer is more favored thermodynamically. With an increase in temperature such that reactions with a higher activation energy become possible or under equilibrium conditions, there is an accumulation of the exo form and decomposition of the endo form of the adduct [5].

In recently published work of Alder [6], Meek [7], and Tate [8], there were interesting data on the effect of substituents in the dienophile on the ratio of the isomeric adducts formed and in a number of cases this led to predominance of the exo isomer.

Due to the fact that diene synthesis of vinyl ethers proceeds at a temperature of not less than 170-175°, the rule on the predominance of the endo form in the adduct is complicated in this case and the condensation of vinyl aryl ethers with cyclopentadiene leads to the formation of an adduct which is a mixture of two isomeric endo and exo forms.



Ar = C_6H_5 (I), p-tert-$C_4H_9C_6H_4$ (II), $C_{10}H_7$ (β) (III)

In an examination of literature data [9, 10], it was noticed that endo and exo isomers, which have similar boiling points, differ in other physical properties; the endo isomer has a higher melting point and a lower solubility. On the basis of this, the adducts (IA) and (IIA), which are crystalline at room temperature, and the higher-melting adduct (IIIA) apparently have the endo configuration, while (IB) and (IIB), which are liquid at

room temperature, and the low-melting adduct (IIIB) have the exo configuration. By using the difficulty of crystallization of endo-2-phenoxybicyclo-(2,2,1)-heptene-5 (IA), we determined its refractive index and specific gravity. It was found that the numerical values of these constants for the endo adduct were higher than for the exo adduct.

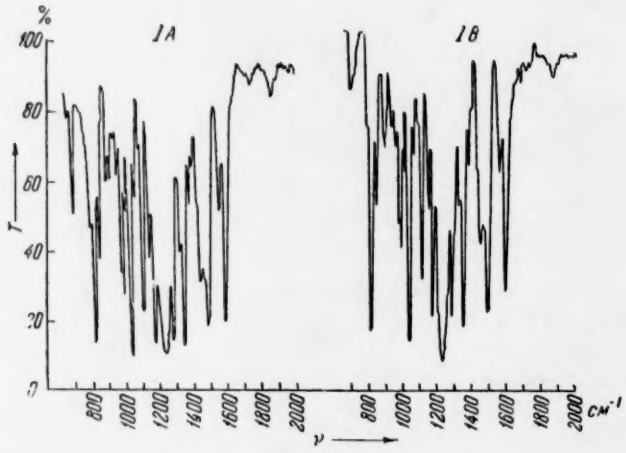


Fig. 1. Spectra of endo (IA) and exo (IB) adducts.

Spectroscopic investigations of the two isomeric forms of adducts (I) and (II) showed that in the infrared spectra of the two forms, the frequencies of the main absorption bands coincided, but each form also had a series of its own absorption bands. For example, the exo adduct (IB) had bands at 1754, 1431, 1381, 1095, 982,

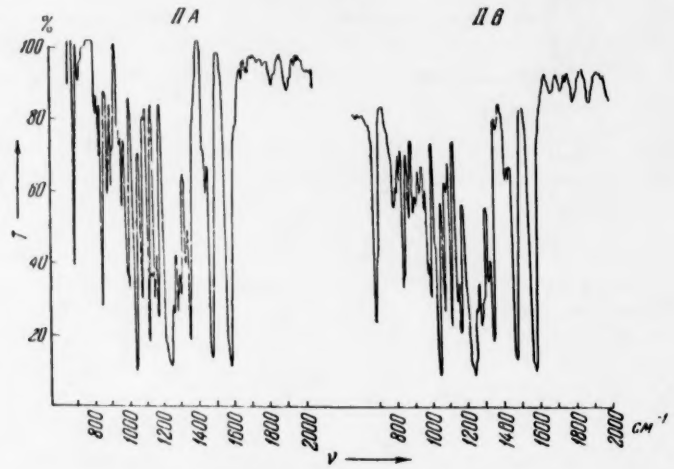


Fig. 2. Spectra of endo (IIA) and exo (IIB) adducts.

804 cm^{-1}, which were absent from the spectrum of the endo isomer (IA); the endo adduct (IIA) had its own bands at 1402, 1095, 923, 807 cm^{-1} (see Figs. 1 and 2). For the analysis of adducts obtained at increasing temperatures for the content of endo and exo isomers, we made use of data obtained from the infrared spectra. The absorption bands peculiar to the two isomeric forms were found to be unsuitable for these purposes due to their low intensity.

TABLE 1

Reaction temp., °C	κ_{ef}	Isomer content of adduct, %	
		exo form	endo form
170	3,10	65	35
180	3,15	67	23
200	3,32	74	26
220	3,44	80	20

A study of the infrared spectra showed that there was a sharp difference in the intensities of the absorption bands present in the spectra of the two forms. This property was used for analytical purposes in the case of phenoxybicycloheptene (I). In the case of adduct (II), this difference was expressed less sharply and therefore it was only possible to make semiquantitative measurements here.

A calibration curve was used for determining the composition of the mixture of the two configurations in adduct (I). For the analysis we chose the absorption band at 685 cm^{-1}, whose intensity differed most for the isomers. As only the effective intensity at the maximum of the absorption band was measured, the calibration curve was far from linear. For construction of the calibration curve (see Fig. 3) we used artificial mixtures containing 0, 50, 67, 83, and 100% of the exo form. The effective intensity (κ_{ef}) was plotted along the ordinate axis and the exo isomer content in percent, along the abscissa. The accuracy of the determination was ±3-4 % at an exo isomer concentration in the mixture of more than 50%, but at a lower concentration of the latter, the accuracy of the determination must have been lower. The analysis results are given in Table 1.

Thus, it was established that the adducts from diene synthesis of vinyl aryl ethers with cyclopentadiene are mixtures of two isomeric forms with endo and exo configurations. Conditions were found for separating these isomers and plotting their infrared spectra, which made it possible to determine the content of the isomers in the mixture. By means of spectral analysis it was shown that with an increase in the reaction temperature there was an increase in the content of the lower-melting isomer (exo form). The observations made it possible to carry out a stereodirected diene synthesis of vinyl ethers with cyclopentadiene.

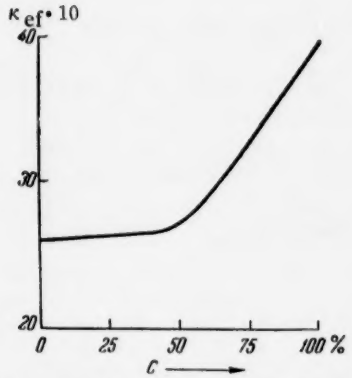


Fig. 3. Graph for determining the exo isomer content of the 1st adduct.

EXPERIMENTAL

Isolation of endo and exo isomers of 2-phenoxybicyclo-(2,2,1)-heptene-5 (I). 2-Phenoxybicyclo-(2,2,1)-heptene-5 was obtained by condensation of vinyl phenyl ether with cyclopentadiene at 165-170°, 180-182°, 197-200°, and 217-220° by the method we described previously [1] and had b. p. 87-88°/1.5 mm; n_D^{20} 1.5500; d_4^{20} 1.0720. Literature data [1]: b. p. 114-114.5°/5 mm; n_D^{20} 1.5500; d_4^{20} 1.0732. The adduct obtained (18.2 g) was left with a seed* at +10-12° for 15-20 hr. The precipitated crystals were collected and recrystallized from methanol until the melting point was constant. We obtained 5.4 g of the high-melting isomer (endo form) with m. p. 39.5-40° (from methanol), b. p. 100.5-101°/2.5 mm; n_D^{20} 1.5531; d_4^{20} 1.0732.

Found %: C 84.34, 84.44; H 7.60; 7.72. $C_{13}H_{14}O$. Calculated %: C 84.36; H 7.58.

The spectrum of the endo isomer is shown in Fig. 1. For the isolation of the exo isomer, 15.5 g of the adduct obtained was left overnight with a seed at 0-2°. The low-melting isomer was separated on a filter with cooling to +4-5°. The remaining filtrate was subjected to fractional freezing 4-5 times and then reprecipitated from methanol until the melting point was constant. The isomer with the exo configuration (1.2 g) had m. p. 3.5-4°, b. p. 106-106.5°/3 mm; n_D^{20} 1.5483; d_4^{20} 1.0652.

Found %: C 84.50; 84.46; H 7.72; 7.78. $C_{13}H_{14}O$. Calculated %: C 84.36; H 7.58.

Isolation of endo and exo isomers of 2-p-tert-butylphenoxybicyclo-(2,2,1)-heptene-5 (II). By condensation of cyclopentadiene and vinyl p-tert-butylphenyl ether by the method we described previously [3], we obtained 2-p-tert-butylphenoxybicyclo-(2,2,1)-heptene-5 with b. p. 137.5-139°/2 mm. Literature data [3]: b. p. 135-135.5°/1.5 mm. The bulk of the adduct obtained crystallized when kept at room temperature for 2 days. The crystalline adduct, to which the endo structure (IIA) was assigned, had m. p. 35-36° (from methanol), b. p. 135-135.5°/1.5 mm; n_D^{20} 1.5332.

*The seed was obtained in the following way: 3 g of adduct was dissolved in 12 ml of dry ether and left at −20-30° until a crystalline precipitate formed. The crystals (0.12 g) were quickly separated from the solution with cooling.

Found %: C 84.29; 84.58; H 9.25; 8.88. $C_{17}H_{22}O$. Calculated %: C 84.24; H 9.15.

The portion of the adduct which did not crystallize at room temperature [exo isomer (IIB)] had m. p. 15.5-16.5° (from methanol), b. p. 134-135°/1 mm; n_D^{20} 1.5327; d_4^2 1.0152; MR_D found 74.08; $C_{17}H_{22}O4F$ calculated MR_D 73.88.

Found %: C 84.27; 83.98; H 9.17; 9.25. $C_{17}H_{22}O$. Calculated %: C 84.24; H 9.15.

Isolation of endo and exo isomers of 2-β-naphthoxybicyclo-(2,2,1)-heptene-5 (III). 2-β-Naphthoxybicyclo-(2,2,1)-heptene-5 with m. p. 65.5-67°, which was obtained by the method we described previously [3], was fractionally crystallized from methanol. We isolated 2 g of product. The endo isomer (IIIA) had m. p. 72.5-73°.

Found %: C 86.60; 86.52; H 6.98; 7.14. $C_{17}H_{16}O$. Calculated %: C 86.40; H 6.83.

The exo isomer (IIIB) had m. p. 64-65.5°.

Found %: C 86.32; 86.28; H 6.95; 6.96. $C_{17}H_{16}O$. Calculated %: C 86.40; H 6.83.

The infrared spectra were plotted on an IKS-14 double-beam infrared spectrophotometer. The spectra were plotted for solutions of the substances in chloroform at a concentration of about 10-15 weight %. The thickness of the absorbing layer was 0.01 cm. The accuracy with which the absorption band frequencies were measure was ±5 cm^{-1}. The percent transmission was measured with an accuracy of ±1%. The spectra were plotted with automatic opening of the instrument slit according to the constant energy law. The spectral width equaled 5-11 cm^{-1}.

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INVESTIGATION OF CATALYTIC PROPERTIES OF PYROPHORIC MANGANESE

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(Presented by Academician A. A. Balandin, February 11, 1960)
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The catalytic properties of metallic manganese have been studied comparatively little up to the present time. In comparing the activities of a series of metallic blacks, O. Schmidt [1, 2] showed that manganese is very active in the low-temperature hydrogenation of ethylene; G. K. Boreskov et al., [3], who studied the catalytic activity of manganese as small granules in the reaction of oxygen with hydrogen, came to the conclusion that manganese has a higher activity than Group VIII metals. Houdry [4] proposed the use of manganese, together with other metals, as a catalyst in the flameless oxidation of fuel. Anderson and Kemball [5] established that a manganese film is completely inactive in the exchange of $C_2H_4 + D_2$ and the cracking of ethane.

The limited number of papers on the catalytic properties of manganese is caused to a considerable extent by the fact that this metal is difficult to obtain in the form of a pyrophoric black. In contrast to Group VIII metals, manganese may be obtained by reduction of the oxides only at temperatures above 1300°; the metal thus formed sinters and loses its activity. Therefore, for the preparation of manganese we used the method proposed by Buntz [6], Prelinger [7], and Schmidt [1, 2], based on the thermal decomposition of manganese amalgam in vacuum. The amalgam was obtained by electrolysis of an aqueous solution of manganous chloride on a mercury cathode. To avoid contact between the black obtained and air, absolute benzene was introduced directly into the apparatus for amalgam decomposition under vacuum and the black was then stored under the same solvent until introduced into the catalysis reactor.

In order to establish the degree of purity of the black obtained, we carried out an additional experiment in which a small amount of manganese was prepared according to the procedure described above, but with mercury containing the isotope Hg^{203} used as the cathode in the electrolysis. By comparing the activities of dilute nitric acid solutions of accurately measured samples of the black obtained and the original mercury, we established that a sample that had been heated at 340-380° in a vacuum of 10^{-6}-10^{-7} mm Hg for 7 hr contained about 0.03 at. % of Hg.

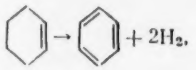
In accordance with literature data, manganese obtained in this way had a high chemical activity. When a mixture of hydrogen and air was sucked rapidly through a layer of a freshly prepared sample there was an exothermal reaction, accompanied by ignition.

We obtained an x-ray diffraction pattern of the manganese black. It was shown that decomposition of the amalgam by the method described yielded α-manganese, which crystallized in a complex cubic lattice of the A-12 type with a parameter $\underline{a}$ equal to 8.923 ± 0.020 A (literature data: a = 8.894 A [8]). It may be considered that in this case a more open lattice was obtained than for metallic manganese obtained by other methods. It should be noted that the x-ray pattern did not contain a single line corresponding to oxides of manganese or other compounds of it. In view of the fact that pyrophoric manganese is oxidized not only by oxygen, but also such oxygen-containing compounds as H_2O, CO_2, and even CO, we were forced to limit our investigation of the catalytic properties of manganese to the dehydrogenation and hydrogenation of hydrocarbons.

Experiments were carried out in a flow system with automatic input of the substance into the reactor. Manganese black (23-23.5 ml*) was introduced into the tube by a method which excluded its direct contact with air; the benzene and air were removed from the system in the cold for 2 hr with electrolytic hydrogen, freed from traces of oxygen by passage through a heated tube with reduced copper. The space velocity for input of the reagent was 0.4. After each experiment, which lasted for 30-40 min, the catalyst was regenerated with hydrogen at the experimental temperature for 1.5-2.0 hr.

Dehydrogenation of cyclohexene. The cyclohexene used in the work was obtained by dehydration of cyclohexanol over magnesium sulfate. In accordance with literature data [9], this catalyst did not produce isomerization of the cyclohexene obtained with the formation of methylcyclopentene. The preparation had the constants: b. p. 80.0-80.5°/736 mm; n_D^{22} 1.4451; d_D^{20} 0.8105. (Literature data [10]: b. p. 83°/760 mm, n_D^{22} 1.44507; d_4^{20} 0.8102).

The reaction was investigated over the temperature range 320-400°. The percent conversion of the cyclohexene was determined from the amount of hydrogen liberated with the assumption that the reaction proceeded exclusively according to the equation



and also from the change in the amount of unsaturated hydrocarbons in the liquid catalyzate (titration with brominating mixture).

The gaseous reaction products were analyzed on a VTI apparatus and it was shown that they consisted of 98.5-99.5% of hydrogen with 0.5-1.5% of saturated hydrocarbons. The ultraviolet absorption spectrum of the catalyzate showed the presence of benzene in addition to the original cyclohexene. Frequencies characteristic of cyclohexadiene were not found.

The catalyst activity did not remain constant during the first 4-5 experiments and reproducible results were obtained only after this. The data obtained are given in Table 1.

TABLE 1

	Freshly prepared catalyst, t = 380°	Catalyst with stabilized activity		
		$t = 322°$	$t = 360°$	$t = 397°$
Conversion on hydrogen, %	60.0	2,0	5,0	13,6
Conversion on unsaturateds, %	40.0	2,5	5,6	13,7

These results show, first, that for freshly prepared catalyst the percent conversion determined by the two methods did not agree; on the given catalyst, hydrogen was formed not solely by dehydrogenation of cyclohexene; secondly, the stabilized catalyst had a considerable lower activity than freshly prepared catalyst; thirdly, the percent conversion calculated by the two methods for the catalyst with a stabilized activity was practically the same. The last fact indicates the absence of irreversible catalysis occurring in parallel with the dehydrogenation as otherwise the percent conversion calculated from titration data would have been higher than that calculated on hydrogen.

We obtained an x-ray diffraction pattern of a catalyst that had been used for eight experiments. It was shown that during operation of the catalyst there was some contraction of the α-manganese lattice (the parameter a became equal to 8.894 ± 0.020 A) and, what was more important, in addition to α-manganese lines, there appeared a large number of bright lines corresponding to manganese carbide with the composition $Mn_{23}C_6$.

*As in Russian. – Publ.

The lattice parameter of this substance, calculated from the diffraction pattern (a = 10.57 ± 0.03 A), agreed accurately with the value given in the literature [11]. In this diffraction pattern also there was not a single line characteristic of any manganese oxide.

Thus, freshly prepared manganese catalyzes not only the dehydrogenation of cyclohexene, but also cracking of the latter with the formation of manganese carbide and an additional amount of hydrogen. We calculated the apparent activation energy of the dehydrogenation of cyclohexene on carbided manganese and found E = 19.3 kcal/mole.

Dehydrogenation of cyclohexane. Since α-manganese crystallizes in neither hexagonal nor cubic face-centered syngony, we could only depend on stepwise dehydrogenation of cyclohexane by an edge mechanism [12].

The starting cyclohexane had the constants: b. p. 79-79.3°/748 mm; n_D^{20} 1.4268; d_4^{20} 0.7785. (Literature data [13]: b. p. 80.75°/760 mm; n_D^{20} 1.4263; d_4^{20} 0.7786.)

It was shown that over the temperature range 440-500° there was very slight dehydrogenation of cyclohexane with the formation of cyclohexene as indicated by the liberation of hydrogen and the appearance of olefins in the catalyzate; however, the yield did not exceed 2.5%, calculated on the cyclohexene formed. The absence of diene and benzene was demonstrated by a spectral method. In this case we also observed that the percent conversion, calculated on hydrogen, was higher than according to titration data. This indicates that part of the cyclohexene formed underwent cracking with the liberation of hydrogen.

Dehydrogenation of ethylbenzene. It seemed interesting to determine whether manganese black was capable of dehydrogenating the side chain of aromatic compounds. We used ethylbenzene with the following constants: b. p. 133.2-133.8°/749 mm; n_D^{20} 1.4966; d_4^{20} 0.8656. (Literature data [13]: b. p. 136.19°/760 mm; n_D^{20} 1.4959; d_4^{20} 0.8670).

It was established that over the temperature range 300-450° manganese is cabable of partially cracking the starting hydrocarbon with the formation of carbon and hydrogen. We arrived at this conclusion on the basis of gas analysis, titration results, distillation of the liquid catalyzate, and also investigation of its infrared spectrum.

It was also shown that over the temperature range 150-215°, pyrophoric manganese hardly catalyzes the hydrogenation of benzene and cyclohexene.

Thus, in the present work it was established that pyrophoric manganese catalyzes the dehydrogenation of cyclohexene with the formation of benzene and simultaneously produces partial cracking of the starting material with the formation of manganese carbide and hydrogen. The activation energy of the dehydrogenation on carbidized manganese equaled 19.3 kcal/mole.

It was shown that manganese hardly dehydrogenates cyclohexane and ethylbenzene and does not hydrogenate benzene and cyclohexene.

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PREPARATION OF MALONIC ACID AND ITS ESTERS BY MEANS OF CARBON SUBOXIDE

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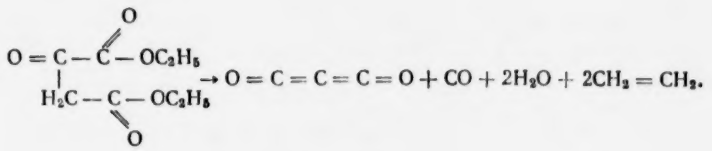
Carbon suboxide is an excellent malonylating agent. It has been used under comparatively mild conditions for the preparation of various substituted malonylamides, pyrazolidines, dialkyl malonates, β-diketones, carbocyclic and heterocyclic compounds, etc. [1-11]. However, for a long time the only methods of preparing carbon suboxide were syntheses from diacid halides of malonic acid and their dihalo derivatives [12, 13] and also pyrolysis of malonic acid [14], malonic ester, and diacetyltartaric anhydride [15, 16].

This was the main obstacle to the practical use of carbon suboxide as a malonylating agent as the preparation methods given above either start from malonic acid and its derivatives or give extremely low yields and involve experimental difficulties.

We developed a new method of preparing carbon suboxide, which consisted of high-temperature pyrolysis of diethyl oxalacetate in a quartz tube. As an experiment showed, the use of catalysts (platinum and silver) promotes contamination of carbon suboxide with carbomethylene, while noncatalytic pyrolysis gives quite a satisfactory yield of carbon suboxide and does not lead to the formation of carbomethylenes as a by-product.

It should also be noted that diethyl oxalacetate is an accessible substance. It can be obtained readily by condensation of ethyl acetate and diethyl oxalate and is produced by our own chemical industry.

Pyrolysis of diethyl oxalacetate proceeds according to the following scheme:



The preparation of malonic acid and dialkyl malonates does not require the isolation of liquid carbon suboxide (b. p. 6-7°). These products are formed in high yield when water or appropriate alcohols are saturated with gaseous carbon suboxide emerging directly from the pyrolysis furnace. Authors who studied the reaction of the suboxide with water suggested that the reaction should be carried out with slight heating [4].

EXPERIMENTAL

Preparation of carbon suboxide by pyrolysis of diethyl oxalacetate. Pyrolysis of acetylenedicarboxylic and oxalacetic acids and acetoxymaleic and diacetyltartaric anhydrides showed that the yield of carbon suboxide could be increased if these substances were introduced into the furnace in acetic anhydride solution. It was found that this was also true for diethyl oxalacetate. Under our experimental conditions, the acetic anhydride

was not pyrolyzed and was subsequently regenerated almost completely. The pyrolysis was carried out in a tubular furnace, 24 cm long. A quartz tube with an internal diameter of 16 mm was fixed in the furnace. At one end the tube was connected to a dropping funnel with a normal pressure leveler and at the other end it was attached to two intermediate volumes, connected in series, for which we used two-necked flasks with coil reflux condensers. The acetic anhydride was collected in the flasks. The flasks were then connected to two successive receivers, filled with absolute ether and cooled with an ice bath. The acetic anhydride solution of diethyl oxalacetate was introduced into the pyrolysis furnace steadily and at such a rate that there was no possibility of carbon suboxide getting past the ether. At 0°, 100 ml of absolute ether dissolves 2.5 g of carbon suboxide. As is known, ether solutions of carbon suboxide are very stable. Even on prolonged boiling of the solution, the concentration continues to remain at a value corresponding to saturation at the boiling point of ether, which is probably explained by the formation of an intermolecular compound of carbon suboxide and ether. The carbon suboxide yield was determined by the anilide method.

Diethyl oxalacetate was pyrolyzed at various temperatures over the range from 650 to 900°. The best results were obtained at a temperature of 850-875°. Over a period of 2 hr, 10 g of diethyl oxalacetate in 70 ml of acetic anhydride was introduced into the pyrolysis furnace at 850°. The carbon suboxide yield was 1.73 g (determined by the aniline method). The average yield of carbon suboxide obtained under the given conditions was 45% of theoretical, calculated on diethyl oxalacetate.

Preparation of malonic acid and some of its esters. The reaction between carbon suboxide, alcohols, and phenol was carried out with heating at 60-70°. As catalyst we used 2-3 drops of HCl. A calculated amount of gaseous carbon suboxide was passed through a capillary tube into water, alcohol, or phenol. After the carbon suboxide had been passed in for 1.5-2 hr, the mixture was heated for another hour and then tested for suboxide by the anilide method. As is usually done, the aqueous solution of malonic acid was evaporated under reduced pressure at 60-65°, while malonic esters were isolated by normal or vacuum distillation.

For reaction with carbon suboxide we used water, methyl, ethyl, propyl, n-butyl, cyclohexyl, and benzyl alcohols, and phenol, which were taken in amounts of 15-20 ml. As a result we obtained: dimethyl malonate with b. p. 179° in 96% yield; diethyl malonate with b. p. 198° in 97% yield, dipropyl malonate with b. p. 228°/764 mm in 94% yield, di-n-butyl malonate with b. p. 249-250°/761 mm in 90% yield, dicyclohexyl malonate with b. p. 193-194°/15 mm in 61%yield, dibenzyl malonate with b. p. 234°/15 mm in 38% yield, diphenyl malonate with m. p. 48° (from ligroin) and b. p. 209° in 69% yield, and malonic acid with m. p. 129-130° in 97% yield.

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TRANSMISSION OF THE EFFECT OF SUBSTITUENTS BY VARIOUS CONJUGATED SYSTEMS

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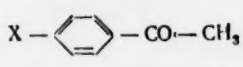
In previous work [1] we showed that the Hammett equation applies to the isotopic exchange of hydrogen. We came to this conclusion as a result of studying the effect of substituents on the rate of isotopic exchange of the hydrogen of the methyl group in para-substituted acetophenones (I).



(I)

As is known, the Hammett equation gives a quantitative relation between the reactivity of benzene compounds and the nature of the substituent in the para or meta positions:

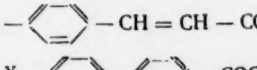
$$\lg \frac{k}{k_0} = \sigma\rho,$$

where k is the reaction rate (equilibrium) constant of the substituted compound, k_0 is the reaction rate (equilibrium) constant of the unsubstituted compound, σ is the constant of the substituent, which depends only on the nature of the substituent and its position in the benzene ring, and ρ is the reaction constant.

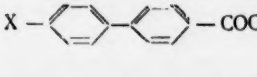
According to Jaffe [2], the reaction constant ρ depends on three factors: 1) the efficiency with which the electronic effect of the substituent is transmitted to the reaction center, 2) the sensitivity of the reaction to a change in electron density at the reaction center, and 3) the reaction conditions.

Thus, by comparing the values of ρ for the same reaction under identical conditions for molecules having different systems of conjugated bonds, it is possible to evaluate quantitatively the efficiency of transmission of the substituent effect through these systems.

In the present work we studied the effect of substituents on the rate of hydrogen exchange of para-substituted benzalacetones (trans) (II) and para-substituted 4'-acetylbiphenyls (III).



(II)



(III)

For this purpose we determined the rate constants of hydrogen exchange at 20°, which were calculated from the equation for a first order reaction for benzalacetone, p-dimethylaminobenzalacetone, p-methoxybenzalacetone, p-nitrobenzalacetone, p-chlorobenzalacetone, p-bromobenzalacetone (see Table 1) and 4'-acetylbiphenyl, 4-nitro-4'-acetylbiphenyl, 4-bromo-4'-acetylbiphenyl, 4-methoxy-4'-acetylbiphenyl, and 4-chloro-4'-acetylbiphenyl (see Table 1). The hydrogen exchange conditions were the same as in the case of para-substituted

acetophenones. The reaction was carried out in absolute ethyl alcohol, containing deuterium in the hydroxyl group, with sodium ethylate as catalyst.

TABLE 1

Ketone	X (substituent)	k_{20}* in sec^{-1}	σ-para*
X—C$_6$H$_4$—CH=CHCOCH$_3$	H	$(5,15\pm0,49)\cdot10^{-5}$	0
	NO_2	$(1,76\pm0,20)\cdot10^{-4}$	0,788
	$(CH_3)_2N$	$(1,01\pm0,14)\cdot10^{-5}$	—0,83
	CH_3O	$(2,48\pm0,26)\cdot10^{-5}$	—0,268
	Br	$(9,72\pm1,50)\cdot10^{-5}$	0,232
	Cl	$(9,70\pm1,50)\cdot10^{-5}$	0,227
X—C$_6$H$_4$—C$_6$H$_4$—COCH$_3$	H	$(3,65\pm0,55)\cdot10^{-5}$	0
	NO_2	$(9,42\pm1,20)\cdot10^{-5}$ **	0,778
	CH_3O	$(3,60\pm0,52)\cdot10^{-5}$	—0,262
	Br	$(6,42\pm0,53)\cdot10^{-5}$	0,232
	Cl	$(6,40\pm0,50)\cdot10^{-5}$	0,227

*The values of σ-para were taken from the table of McDaniel and Brown [4].

**The value $k_{20^\circ} = 6.69 \cdot 10^{-5}$ sec^{-1} was given previously [1], but it was determined more accurately in the present work.

The relations of the logarithm of the rate constant for hydrogen exchange of para-substituted benzalacetones (Fig. 1) and para-substituted 4'-acetylbiphenyls (Fig. 2) to the substituent constant σ-para were linear. Thus, it was shown that the Hammett equation is obeyed in the hydrogen exchange of para-substituted benzalacetones and para-substituted 4'-acetylbiphenyls, as for para-substituted acetophenones. The values of the

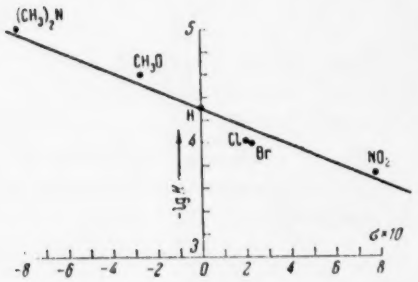


Fig. 1.

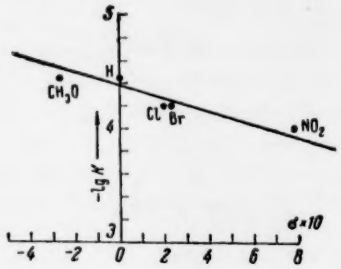


Fig. 2.

constants ρ were calculated for all the systems we investigated and were found to equal 1.6 for the acetophenone system (I), 0.8 for the benzalacetone system (II), and 0.4 for the 4'-acetylbiphenyl system (III).

In the ketones examined, the substituent was separated from the reaction center by various systems of conjugated bonds, namely, a benzene ring, a double bond conjugated with a benzene ring, and the biphenyl system.

If we take the value of ρ for the acetophenone system as equal to unity, we then obtain relative values of ρ of 1 for the acetophenone system (I), 0.50 for the benzalacetone system (II), and 0.25 for the 4'-acetylbiphenyl system (III).

The data obtained are in good agreement with the results presented by Berliner and Liu [3], who calculated the relative values of ρ for the hydrolysis (in 88.7% ethanol) of ethyl esters of substituted benzoic ($\rho_{rel} = 1$),

cinnamic (ρ_{rel} = 0.53), and biphenylcarboxylic acids (ρ_{rel} = 0.24). However, the same authors derived relative values of ρ for the dissociation of the corresponding acids: benzoic (ρ_{rel} = 1), cinnamic (ρ_{rel} = 0.47), and biphenylcarboxylic (ρ_{rel} = 0.37), and these values differ somewhat from the relative values of ρ from the hydrolysis of the esters and also from the data we obtained for the isotopic exchange of hydrogen.

Thus, from a comparison of the relative values of ρ we obtained for the isotopic exchange of hydrogen of para-substituted acetophenones, benzalacetones, and 4'-acetylbiphenyls, and considering that the steric factors in these molecules in the given reactions are identical, it is possible, following Berliner [3], to draw the conclusion that in hydrogen exchange, a double bond conjugated with a benzene ring transmits only 0.50 of the electronic effect of the substituent and the biphenyl system, only 0.25 of this effect in comparison with one benzene ring.

EXPERIMENTAL

The hydrogen exchange of the ketones studied was carried out in absolute deuteroethanol (containing 8-10 at. % of deuterium in the hydroxyl) with sodium ethylate as catalyst (as a solution in deuteroethanol). The sodium ethylate concentration in the reaction solution equaled 0.00036 N. A large excess of deuteroethanol was used, namely, 200-800 moles of deuteroethanol to 1 mole of ketone, depending on the solubility of the ketone. Special experiments showed that under the conditions we chose the rate of hydrogen exchange was independent of a change in the amount of deuteroethanol by a factor of 2-4.

The hydrogen exchange was stopped by cooling to −80°, when the ketones precipitated. Only in the case of benzalacetone and p-chlorobenzalacetone was the reaction mixture poured into water (a water volume 25 times greater than the sample volume) to stop the reaction.

The deuterium content was determined by the drop method [5].

The authors consider it their duty to thank Professor A. I. Shatenshtein, Ya. M. Varshavskii, E. A. Yakovleva, and O. P. Gei for great help in mastering this method.

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MICROBIOLOGICAL DEACETYLATION OF 21-ACETATES OF CORTICOSTEROIDS

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Microbiological conversions of steroids have attracted great attention from investigators due to their great practical value in the synthesis of cortisone and its analogs. At the present time these conversions include oxidation–reduction processes involving carbonyl and hydroxyl groups, hydroxylation of the steroid nucleus and the side chain, dehydrogenation, elimination of the side chain, and cleavage of the rings of the steroid [1]. In the brilliant work of Peterson and his co-workers it was shown that the hydroxylation of steroids containing acetoxy groups by means of imperfect fungi is accompanied by deactylation of these compounds [2]. On the other hand, some bacteria, for example, Corynebacterium simplex, are capable of dehydrogenating 21-acetates of corticosteroids without hydrolysis of the acetyl group [3].

In studying problems in the microbiological dehydrogenation of corticosteroids, we observed that the culture we isolated (VNIKhFI-1), which in morphological and biochemical properties belonged to the group Bacillus megatherium, was capable of deacetylating cortisone acetate to free cortisone. Further investigations showed that this deactylation was specific for 21-acetates of steroids containing a dihydroxyacetone chain (cortisone, Reichstein's substance "S", 4,5-β-dihydrocortisone, and Δ^1-dehydrocortisone). In the case of desoxycorticosterone acetate (a ketol chain instead of a dihydroxyacetone chain), the deacetylation proceeded slowly and partially. Acetoxy groups in positions 3β, 11α, and 17β were not hydrolyzed. Our strain produced no other conversions such as hydroxylation, reduction, dehydrogenation, etc., at least in the case of corticosteroids. In this connection, the recently published work of Herzog et al., [4] is particularly interesting as they showed that the strain of B. megatherium that they isolated (Schering 41 ATCC No. 13368) has the power to introduce 15β-hydroxyl group into Reichstein's substance "S" and progesterone and also to reduce the $\Delta^{1,2}$ double bond in dehydrocortisone and dehydrocortisol. At the present time we are studying the behavior of our strain towards steroids which contain no acetoxy group.

EXPERIMENTAL

The deacetylation with the strain VNIKhFI-1 was carried out in a medium consisting of yeast extract (0.5%) and glucose (0.5%). The experiments were carried out in a glass fermenter fitted with a stirrer, immersion heater, and a tube for the input of sterile air. The temperature (28°) and air input rate were regulated automatically. A volume of air equal to the volume of the medium was introduced per minute.

Under aseptic conditions, the fermenter was charged with culture liquid containing a washing of the strain VNIKhFI-1, grown for 48 hr on agar plates. Then an acetone solution of the steroid (1 g of the latter to 45 ml of acetone and 8 liters of culture liquid) was added through a dropping funnel. The duration of the deacetylation process for different steroids was varied from 24 to 48 hr. The end of the process was determined by paper chromatography (formamide–benzene system).

The reaction product was extracted with chloroform. After removal of the latter, the residue was recrystallized from an appropriate solvent. All the substances obtained by deactylation were found to be identical with authentic samples of the corresponding steroids according to infrared spectroscopic data.

Cortisone acetate. The deactylation of 1.00 g for 24-28 hr yielded 0.81 (90% of theoretical) of free cortisone with m. p. 226-227° (from alcohol). $[\alpha]_D^{20°}$ = + 215° (0.5% solution in alcohol). λ_{max} = 238 mμ, log ε = 4.406.

Δ^1-Dehydrocortisone acetate (prednisone acetate). 1.00 g of a preparation was subjected to the fermentation process for 24-28 hr. The yield of free Δ^1-dehydrocortisone (prednisone) was 0.65 g (73% of theoretical). It had m. p. 228.5-230° (from isopropyl alcohol), $[\alpha]_D^{20°}$ = +178° (1% solution in dioxane), λ_{max} 238 mμ, log ε = 4.193.

Acetate of Reichstein's substance "S". The process was carried out for 24-28 hr. From 1.00 g of starting material we obtained 0.83 g (93% of theoretical) of free hormone. It had m. p. 210-212° (from acetone), $[\alpha]_D^{20°}$ = + 124° (1% solution in dioxane), λ_{max} 240 mμ, log ε = 4.24.

4,5β-Dihydrocortisone acetate. 1.00 g of steroid was subjected to microbiological deacetylation for 48 hr. We obtained 0.60 g (67% of theoretical) of dihydrocortisone. It had m. p. 227-229° (from butyl acetate), $[\alpha]_D^{20°}$ = + 88.8° (1% dioxane solution).

Desoxycorticosterone acetate. When the fermentation process was carried out with 1 g of preparation, according to paper chromatography data the substance obtained was a mixture of desoxycorticosterone and its acetate. When acetylated with acetic anhydride in pyridine, the substance isolated (0.5 g) gave 0.6 g of desoxycorticosterone acetate. It had m. p. 155-156° (from acetone), $[\alpha]_D^{20°}$ = + 183° (1% solution in chlorform), λ_{max} = 240 mμ, log ε = 4.205.

Δ^5-Pregnenol-3β-one-20 acetate was recovered unchanged (60% yield) after fermentation for 48 hr. It had m. p. 146-147°, $[\alpha]_D^{20°}$ = + 21.9° (1% solution in alcohol).

11α-Hydroxyprogesterone acetate was recovered in the unhydrolyzed state (76% yield) after a fermentation process for 48 hr. It had m. p. 173-175°, $[\alpha]_D^{20}$ = +138° (1% solution in acetone), λ_{max} = 240 mμ, log ε = 4.20.

Testosterone acetate and propionate did not undergo microbiological deacetylation either and were recovered after 48 hr (50 and 65 % yield, respectively).

In all of the last four cases, no free hydroxysteroid could be detected by paper chromatography.

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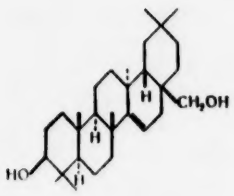
ERRATUM

Proceedings of the Academy of Sciences of the USSR, Chemistry Section
Vol. 129, November-December, 1959, p. 955

In formula V, the hydroxymethylene group should be at the 17th, and not at the 22nd, carbon atom.



SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.– Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.